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CHEMISTRY OF
SPECIFIC, SELECTIVE AND SENSITIVE REACTIONS

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By

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PREFACE

During the past twenty-five years, analytical methods based on the properties and reactions of the substances to be detected or identified have been improved to a greater extent than in all the preceding years. This is shown by the steadily increasing number of new methods devised, by the many improvements and simplifications of older methods, and by the scientific explanations of the details of analytical procedures. This development in breadth and depth, as well as the coincidental development of instrumental methods of analysis has been stimulated by the idea that the goal of analytical work must be the identification and determination of the smallest possible quantity of a substance, even in the presence of other substances, using a minimum of material, time and working efforts, regardless of the technique involved. Thus, the greatest importance must be given to the specificity, selectivity and sensitivity of the analytical processes.

The present book, based on many years of research and study of the literature, is an attempt to summarize our knowledge of the scientific background of the specificity, selectivity and sensitivity of analytical procedures. This indicates that the book is not a mere bibliography of chemical methods of identification and determination. The immediate object is to discover such regularities and rules as govern specificity, selectivity and sensitivity by examining the details of analytical procedures. Therefore, the mechanism of chemical reactions, the composition and constitution of the reacting substances and the products obtained, as well as the influence of the conditions under which the reactions take place, must be studied. Furthermore, the relationship between solubility, color, fluorescence, *etc.*, and the constitution of compounds must be considered. Such an approach to analytical processes makes it necessary to pay careful attention to other fields of chemistry. It is obvious that pertinent material cannot be obtained from abstracts of analytical papers alone. Important facts and observations are often presented as apparently unimportant parts, sometimes even as footnotes, of original papers. Frequently, it is the interpretation of certain data by the author of a paper, or by other authors in later papers on the same or a similar subject, which leads to interesting and important conclusions. Publications in the field of inorganic and organic chemistry, colloid chemistry, photochemistry, *etc.*, may also contain facts which are valuable

in the study of specificity, selectivity and sensitivity. · It is rather difficult to obtain such material from papers which are not primarily analytical, but it is indispensable to at least make an attempt to do so. When reviewing the chemical literature from this standpoint, the close connection between analytical chemistry and other fields of chemistry is shown in still another way. In analytical papers we frequently find experimental results whose importance may exceed the analytical interest. Thus, when elaborating analytical processes, new compounds have been discovered, some of which, by their formation, composition, constitution and characteristics, are of great importance in the chemistry of complex compounds and in physicochemical research. Frequently, metallo-organic compounds which are used analytically force us to consider the isomerism, tautomerism and resonance of organic compounds. The efforts to obtain metallo-organic compounds with somewhat different properties have often resulted in the synthesis of new organic compounds, and the methods of preparing organic reagents have also been improved. Many catalytic effects and induced reactions were first observed in analytical research. Finally, the verification of reaction anomalies observed in the course of analytical processes have often led to important studies of solubility, the influence of conditions under which substances are formed, and colloidal phenomena. Thus, studies and researches on the cause of specificity, selectivity and sensitivity of analytical procedures deserve attention for the following reasons: they extend the scientific basis of analytical chemistry; they furnish important points of reference and orientation in the research for new, analytically applicable reactions; and they initiate and stimulate work in many special fields of chemistry. In these studies and investigations, such a great mass of experimental chemical facts and data can be encountered, that, to call their collection and classification the "Chemistry of Specific, Selective and Sensitive Reactions" may be justified.

The object of this book is to present such a collection and classification, and, therefore, to serve as a guide, awaken interest in, and stimulate studies of, the chemistry of specific, selective and sensitive reactions. The author is conscious of the fact that his exposition and interpretation of a special field hitherto unrecognized as such cannot be complete. In addition to the lack of a model which could serve as a guide, it was impossible, even with great effort, to cover all the material scattered through the chemical literature. The author must also admit that he considers the chemistry of specific, selective and sensitive reactions experimental chemistry, and that, therefore, he has stressed the experimental side principally, even at the risk of slighting some theoretical aspects.

The material presented is divided into twelve chapters, some of which have the same, or somewhat altered, titles as the chapters in the theoretical part of my "Qualitative Analysis by Spot Test." Of course, portions originally present in that book had to be revised and enlarged. Thus, in Chapter III, relating to the types of complex compounds which are of importance as reagents and reaction products, organic molecular compounds are discussed as well as non-stoichiometric coordination products which form lakes and adsorption compounds. In Chapter IV it is shown that there are various types of reaction masking, and also that the reverse process, demasking, is of analytical importance. In Chapter V, on the enhancement of reactivity, the different kinds of catalytic and induced reactions are discussed and many examples given. Chapter VI deals with organic reagents, which have acquired such importance lately that a number of monographs on this subject have been published. In the treatment of this subject, I laid greatest stress on the effect of certain structural groups in the molecules of the organic reagents, on the influence due to other groups in the molecules upon the properties of such structural groups, and on the importance of the effects of coordination. As the properties of structural groups in organic compounds are of great importance in organic analysis, Chapter VII contains material connected with this subject. Chapters VIII and IX deal with regularities in solubility and the influence of certain groups, when present in organic and metallo-organic compounds, on solubility in water and organic solvents. Chapter X shows the importance of surface effects in specificity, selectivity and sensitivity of reactions. In this chapter, the author has attempted to treat in an exhaustive manner the important relationships existing between analytical and colloidal chemistry. In Chapter XI it is made evident that regularities and anomalies in the course of precipitation reactions are connected with the genetic formation of materials and that therein topochemical reactions also play a role. The final chapter (XII) deals with fluorescence and photochemical reactions employed as the basis of specific, selective and sensitive tests. Throughout the book a great effort has been made to include literature references. Nearly all chapters contain critical remarks pertinent to the subject. Frequently, it is shown that the chemistry of analytical methods described in the literature can by no means be considered as settled, but needs revision. This, as well as the inclusion of many previously unpublished observations by the author should stimulate research work in the field of specific, selective and sensitive reactions.

The contents of this book and the method of its presentation were chosen with three groups of readers in mind. The first group consists of those who wish to know the chemical basis of many modern analytical

procedures. The second group is made up of those who are actively engaged in research in analytical chemistry or in related fields. The third group includes those interested in experimental chemistry as a part of science which is still a fertile field for the trained and alert investigator.

The author began his preparatory studies long before the war, but the laboriously gathered material was lost during his flight from Europe. In 1941 I was able to resume these studies as a result of an invitation by the Brazilian government to become a staff member of the Department of Mineral Production of the Ministry of Agriculture. Therefore, I wish to express my appreciation to His Excellency, the Minister, Dr. Daniel de Carvalho, and to Dr. Mario da Silva Pinto, General Director of the Department, who, from the beginning of my activities in Rio, have given complete cooperation and encouragement. I must also thank Dr. A. Girotto, Director of the Chemical Laboratories of the Department, for his warm interest in my research work.

I wish to acknowledge gratefully the many helpful suggestions I received from Prof. Dr. H. W. Zocher and his collaboration in experimental work. I also express my thanks to Dr. G. B. Heisig, on sabbatical leave from the University of Minnesota, who has cooperated in researches, some of which have been included in this book, and for his aid in correcting the proofs. To Dr. W. A. Hynes, of Fordham University, I am indebted for his careful and thorough elaboration of the Subject Index, which forms an important part of this monograph as a useful guide for its consultation.

My especial thanks go to Dr. R. E. Oesper for his translation of the German manuscript, for a great deal of technical advice and for the patience he showed, even with last minute changes. His achievement, going far beyond the task of a translator, is the result of his deep understanding of the aims of this work.

Last, but not least, I wish to thank my many colleagues and students in almost every part of the world, who have enthusiastically collaborated with me during the past twenty-five years; the results of this collaboration, to a great extent already published in numerous papers, are included in this book. When reading this volume, they will find that, in addition to such earlier publications, many ideas and considerations which arose from our discussions regarding our efforts in developing the spot test technique, now appear in an elaborated form among the basic parts of this "Chemistry of Specific, Selective and Sensitive Reactions."
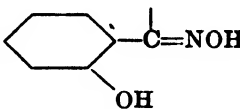
FRITZ FEIGL

Rio de Janeiro, May 1949

CONTENTS

General Comments on the Analytical Usefulness of Chemical Reactions

The function of analytical chemistry is to present trustworthy methods and procedures for detecting and accurately determining elements and characteristic compounds, either alone or in mixtures. Consequently, it is an auxiliary science for all branches of physical research and technology that present questions as to the structure, transformation, and distribution of substances. These inquiries give rise to a profusion of the most varied problems, and their systematic treatment and intelligent solution through analytical chemistry is possible only if the methodology of its procedures and their study is placed on a secure scientific basis.

The multiplicity of problems in the most diverse fields whose solution is achieved or facilitated by chemical analysis is not determined solely by the difference of the elements, and their compounds. This is apparent from the mere fact that the number of the elements and compounds to be detected and/or determined is far fewer than the available methods.[1] The chief reason for this disproportion is that practically always account must be taken of the presence of attendant materials, whose kind and quantity may vary between wide limits. A reaction that is perfectly reliable for the detection or determination of a particular material in a certain reaction environment may fail completely if it is applied under other circumstances. Consequently, the choice of suitable methods must be made in the light of the possible variations in the kind and quantity of the accompanying materials. Furthermore, acceptable analytical methods must permit the detection and/or determination of both large and small quantities, with a reasonable expenditure of time, reagents, and attention.

Chemical analysis invariably rests on the possibility of converting the substance to be detected or determined into another characteristic form of combination. Therefore, it is based eventually on the possibility of changing the combining form of certain atoms or groups of atoms. Analytical chemistry must make an intelligent choice from the numerous chemical reactions involving such changes. It is obvious that the demands on chemical reactions with respect to their analytical applicability are quite different when the problem at hand is qualitative, rather than quantitative.

If the reversible transformation of compound A into compound C by interaction with compound B is represented by the general equation

$$A + B \rightleftharpoons C$$
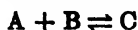
[1] This applies of course only to inorganic compounds.

a quantitative determination demands: the rapid and practically complete conversion of A into C; the exact stoichiometric formulation of this conversion; the possibility either of isolating the reaction product C (or of converting it into a compound whose weight or volume can be measured); or of determining the quantity of B consumed. A chemical change, therefore, is of value for quantitative analysis if, with practically *complete conversion* of the material to be determined, *it is possible to measure one of the reaction products or one of the reactants, and in a reasonable time.*

Quite different conditions must be fulfilled if a reaction is to be used for qualitative purposes. In this case, the measurability is not the essential factor; it must be possible *to observe the reaction easily, indubitably, and in the shortest possible time.* It is not necessary that the material to be detected be converted *completely* into a new compound; transformation of a trace will suffice if the reaction occurs with sufficient speed and results in a product that is readily perceived. In principle, it makes no difference whether this product is a slightly soluble precipitate, a gas, or a soluble material exhibiting a characteristic color or fluorescence. Nor is it necessary that the stoichiometric aspects of the reaction be known; for qualitative purposes a knowledge of the composition of a reaction product or its transformation into a definite compound is, of course, always desirable, but not absolutely essential for practical purposes. There are excellent methods of detection in which the nature of the compound formed is not known with certainty. The latitude in the analytical application of chemical reactions for detection purposes is so great that it is not even necessary that the material to be detected appear as a visible or tangible participant in a given transformation; cases are known in which the material reveals its presence solely by its catalytic effect on a reaction which otherwise would proceed very slowly. In fact, numerous examples demonstrate that such changes, in which a catalytically accelerated reaction serves to reveal the catalyst, have special analytical significance. The same is true, also, for those instances in which a second reaction, not independent of the first, is initiated or "induced" by a reaction of the material to be detected. Adsorption processes and topochemical effects belong in this category. Such secondary reactions, which almost always are undesirable concomitant phenomena in quantitative analyses may be very welcome in qualitative work if they lead to the easy recognition of the occurrence of the primary reactions. Relevant instances will be cited and discussed in the later chapters.

The most important requirement of chemical reactions used for qualitative purposes is that they permit a practical, rapid detection of

the smallest possible quantities at the highest possible dilution. This characteristic is termed **sensitivity.** Furthermore, it is desirable that any other materials present interfere with the detection to as small an extent as possible. This characteristic is termed **selectivity,** and in extremely favorable cases is known as **specificity.** The characterization of the sensitivity by definite numerical values, and the definition and significance of specificity and selectivity will be discussed in detail in Chapter II.

When considering *per se* a chemical reaction that is the basis of a test, it is never permissible to make statements regarding sensitivity, specificity, or selectivity, as though such figures are characteristic data of a reaction, or of products of a reaction, comparable to values such as equilibrium constants, solubility products, *etc.* Experience has shown that the sensitivity, specificity, or selectivity of a reaction are affected by the prevailing conditions and the medium in which the reaction occurs. Among such determinants are: temperature, pH of the solution, degree of dispersion of the reactants, presence of co-solutes, *etc.* The importance of considering not only the purely chemical reaction as such, but also the reaction conditions under which a test is made, is proven by the fact that extremely few test reactions are absolutely infallible. Sometimes, materials that apparently are quite indifferent may delay, or even prevent entirely, the formation of the reaction product normally expected. This effect is particularly likely to be encountered in dilute solutions of the material to be detected. On the other hand, it is often possible, by suitably altering the reaction medium, to secure incontrovertible tests with a reaction which is ordinarily not specific. Furthermore, the discernibility of typical reaction products, and therefore the sensitivity of a test, can often be improved considerably by proper expedients. *The analytical value of a chemical reaction (or of a reagent) is determined primarily by whether its application leads to tests of maximum certainty and sensitivity under defined and easily attainable test conditions.* Consequently, it is much more correct to apply the terms sensitivity, specificity, or selectivity to a test, rather than to a reaction, because the term "test" necessarily includes the test conditions. If, following common practice, the terms: specific, selective, or sensitive reaction, are used in this text, it must be stressed that these characterizations do not apply without limit to a reaction as such; *i.e.,* to the chemical phenomenon that can be formulated chemically and stoichiometrically. Invariably, the description refers to the "detection reaction," *i.e.,* to the reaction conducted under specific experimental conditions.

The analytical value of a reaction not only decides its use in qualitative analysis, but is also significant for its utilization in quantitative

analysis, especially in the analysis of mixtures. There are, however, many more devices and possibilities for attaining specificity or selectivity of reactions and reagents in qualitative analysis. The greater freedom in the choice of more suitable reagents, in modifications of the procedure and, last but not least, in the easier inhibition of possible disturbances due to accompanying materials, are of the greatest importance in methods of detection.

When evaluating chemical reactions for their possible use in analysis, it is always necessary to remember that the ability to formulate the chemistry of the reaction stoichiometrically, or at least to state it in known empirical terms, is not of exclusive significance. The reaction conditions as a whole must be taken into account. The production of new materials is always the net result of the combination of all the chemical and physical factors active during the process of formation. Consequently, changes in the conditions surrounding the formation of the product may exert a considerable effect. Hence, practical experience and strict adherence to a definite procedure play a significant role in the successful accomplishment of both qualitative and quantitative analysis. This is by no means to be taken as implying that analytical chemistry is no more than a collection and orderly arrangement of recipes. On the contrary, it is nearly always possible to give a theoretical basis for the methods and operations that have been prescribed in analytical procedures. A knowledge of the relation between the theory and practice of chemical analysis is of didactic value in that it brings out the many-sided connections of chemical information and puts analytical operations on a sound scientific foundation. Such knowledge is far more important in every piece of research that has as its objective the improvement of existing analytical methods or the discovery of new ones, or the adaptation of known methods to the solution of special problems. The advance of qualitative analysis particularly demands the review of all those bits of chemical knowledge that give promise of eventually providing tests which are more sensitive and of the greatest possible unequivocality. Accordingly, it is necessary to consider the theoretical bases of the chemistry of specific and selective reactions, so that by sensible applications of such fundamentals the investigator, to a degree, is rendered independent of purely empirical hit-or-miss experiments, and is in a far better position to embark on a well-planned course of research. It is necessary to take into the picture provinces of chemistry that for a long time have not been seriously considered in this connection, or that were regarded as too remote from the field of analytical chemistry to be worthy of attention.

This book will deal with the scientific foundations of specific, selective,

and sensitive reactions for use in analysis. The term "reaction" is used in the broad sense, thus including reaction conditions, *etc.* Particular emphasis is placed on **spot test analysis**, which is a method of qualitative analysis recently adapted also to quantitative determinations. This method of analysis is based on the principle of accomplishing a chemical reaction within the volume of a single drop, and has the goal of detecting, in this simple way, the largest possible number and variety of inorganic and organic materials.[1] In a procedure of this kind, which has both microchemical and semimicrochemical objectives, tests of the highest possible unequivocality are obviously necessary, and all possibilities must be explored to attain tests of maximum sensitivity. Since spot test analysis is a relatively young branch of analytical chemistry, the discovery of new specific, selective, and sensitive reactions was of such vital importance that new guiding ideas were necessarily sought out. Otherwise the developers of this province would have had to rely on pure empiricism. The theoretical and experimental foundations taken into account by the author when he developed spot test analysis, and the necessary concomitant investigation of new reactions and aids that can be used for such analytical purposes (organic reagents, catalyzed and induced reactions, photoreactions, *etc.*) will be discussed in this book. Much that will be given here is of basic importance for qualitative analysis in general. Such discussions will also be valuable with regard to quantitative analysis, in which logical use is often made of new chemical reactions that have been described initially as qualitative tests. The text will comprise the following main topics, which are discussed in detail chiefly in Chapters II–XII.

The material that is characterized by a few catch-words in II to XII has been taken from various provinces of chemistry. It will be considered, in the chapters that follow, from the standpoint of its significance with respect to the problems of the specificity, selectivity, and sensitivity of analytical reactions. For such treatment it was necessary to collect a mass of material that hitherto has remained outside the domain of interest to the analytical chemist. However, the author deems the discussion of this material an indispensable part of any adequate treatment of the topic "Chemistry of the specific, selective, and sensitive reactions."

[1] An extended treatment on the use of spot tests in inorganic and organic analyses, together with their application in various technical problems, will be found in the author's Qualitative Analysis by Spot Tests, 3rd Eng. Ed., Elsevier Pub. Co., New York, 1946. This will be referred to hereafter simply as Spot Tests. An introduction to spot test analysis, with special emphasis on its pedagogical aspects, is given in the author's Laboratory Manual of Spot Tests, Academic Press, New York, 1943. This will be referred to as Laboratory Manual.

The Characterization of Chemical Tests by Sensitivity, Selectivity, Specificity, and Limiting Proportion. . The Role of Reaction Conditions

The appraisal of an analytical test is made in terms of its sensitivity, and its certainty in greater or lesser degree. For a long time, the term sensitivity had been given quite different meanings. Sometimes it signified the smallest quantity of detectable material; sometimes the relation between the quantity of the material that can be detected and that of the solvent present; and frequently it was applied only to a reagent and not to a reaction.

A knowledge of the smallest quantity of detectable material determines the evaluation of the sensitivity of a test. Therefore, the author proposed the term *"identification limit,"* which has now been almost universally adopted. This is defined as the minimum quantity of material, expressed in millionths of a gram (micrograms, gamma, γ), which can be clearly revealed by any reaction or method, no matter what the volume.[1] The mere statement of the identification limit obviously reveals much in many questions of analytical interest. However, this figure is not entirely adequate for a perfectly unequivocal appraisal of the sensitivity, because, obviously, it makes a difference whether 1γ of a material may be detected in 1 mm.[3], in 5 ml., or in 1 liter of a solution. For practical purposes, the knowledge of the volume of liquid in which a test can still be clearly obtained, is of no less importance than a knowledge of the identification limit. The erroneous conclusions concerning the active range of a test that follow from a one-sided consideration of the detection limit is demonstrated by the following example. By adding cesium sulfate, which forms the difficulty soluble cesium aluminum alum,[2] it is possible, under the microscope, to detect 0.35γ aluminum in a microdrop (0.001 ml.) of an aluminum solution. This quantity is, of course, very small, but, if the volume in which this test is carried out is considered, the dilution is approximately 1:2900. In other words, the aluminum is revealed by the formation of alum in a micro drop of a solution only if the latter contains at least 0.03% of this element. This statement is not to be taken as a disparagement of this microchemical test, because it is obviously of great importance that a test can be accomplished at all in so small a volume (1 mm.[3]). However, this example (along with other microchemical tests involving formation of crystalline

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[1] F. FEIGL, *Mikrochemie* 1, 4 (1923).

[2] H. BEHRENS, *Z. anal. Chem.* 30, 160 (1891).

precipitates) plainly demonstrates that certain tests are limited by the concentration of the material to be detected. If the given reaction were the only test available for aluminum, it would always be necessary to bring more dilute aluminum solutions up to the concentration demanded by the cesium reaction. The important practical requirement that the detection of materials should, as far as possible, be independent of their concentration, makes it imperative that tests be expected to reveal not only absolutely, but also relatively, small quantities of materials. The identification limit, consequently, is properly correlated only by the statement of the prevailing dilution.

When considering chemical tests, the identification limit can be regarded as the expression of the *quantity sensitivity*, and its ratio to the volume as the expression of the *concentration sensitivity*. Accordingly, the detection of aluminum by the formation of cesium aluminum alum is quantity sensitive but not concentration sensitive. In the broadest sense, a test should be described as sensitive only when it is both quantity and concentration sensitive; in other words, if its identification limit is low even at great dilutions. Tests having these characteristics are greatly preferred in spot test analysis.

The degree of dilution prevailing at a given identification limit (originally termed "sensitivity limit" by the author) has been aptly called *"concentration limit"* by Hahn,[3] and its reciprocal value *"dilution limit"* by Heller.[4] The concentration limit can be given either as the actual concentration expressed, for instance, in γ/ml., or it may be stated as the ratio of unit weight of the material detected to the quantity of solvent. The dilution limit is the reciprocal of the concentration limit. These values may be calculated by the simple expressions:

$$\text{Conc. limit} = \frac{\text{Ident. limit (in } \gamma)}{\text{Vol. of sol. (in ml.)}} = 1 : \frac{\text{Vol. of sol. (in ml.)} \times 10^6}{\text{Ident. limit (in } \gamma)}$$

$$\text{Dil. limit} = \frac{\text{Vol. of sol. (in ml.)} \times 10^6}{\text{Ident. limit (in } \gamma)}$$

It is easy to calculate the concentration limit and the identification limit by this equation. For example, if 0.1γ can be detected in the following volumes of test solution, the corresponding limits are:

Volume corresponding to. 0.1γ	Concentration limit		Dil. limit
	either	or	
10 ml.	0.01γ/ml.	$1:10^8$	10^8
1 ml.	0.1γ/ml.	$1:10^7$	10^7
0.05 ml.	2γ/ml.	$1:5 \times 10^5$	5×10^5
0.001 ml.	100γ/ml.	$1:10^4$	10^4

[3] F. Hahn, *Mikrochemie* **8**, 75 (1930).

[4] K. Heller, *Mikrochemie* **8**, 141 (1930).

The quantity 0.1γ is, of itself, an extremely small weight of material, and if this minute quantity can be detected in 10 ml., or 1 ml., or even 0.05 ml., the term "very sensitive" can justifiably be applied to a reaction which succeeds even at these high dilutions. But this is not the case when 0.1γ is present in the volume of one micro drop (0.001 ml.) where it forms only a 0.01 % solution, which certainly is not a high dilution.

On the other hand, neither is the mere declaration of the dilution enough, for if no more is stated about a test than that it can be carried out successfully at a given dilution, say 1:10,000, no information has been given concerning the volume of this highly diluted solution in which the test is accomplished. Only when this latter figure has also been supplied is it possible to apply the foregoing formula and to calculate the corresponding identification limit from the dilution and volume of the test solution. For example, if a test succeeds in 5 ml. of a solution whose dilution is 1:100,000, then by the foregoing equation the identification limit is:

$$1:100,000 = 1:\frac{5 \times 10^6}{X}$$
$$1:100,000 = X:5 \times 10^6$$
$$X = \frac{5 \times 10^6}{10^5} = 50\gamma$$

Consequently, if a test gives a positive response in 5 ml. of a solution, whose dilution is 1:100,000, and fails when a smaller volume of the test solution is taken, the corresponding identification limit is 50γ. A test of this caliber cannot be regarded as sensitive. If, on the contrary, a solution of this same dilution gives a positive test when tried as a spot reaction (0.05 ml.) then the test is really sensitive, as the corresponding identification limit is 0.5γ.

The foregoing calculations demonstrate that the sensitivity of a test must never be judged solely by either the smallness of the identification limit, or the high value of the dilution limit. The real sensitivity of a test is defined or accurately characterized by stating both. *Only those tests can be considered sensitive*, using the term in its widest sense, *which are both quantity and concentration sensitive.* In other words, the identification limit must be low and the dilution limit high.[4a]

It must be noted that the identification limit and the concentration limit of an analytical test, unlike chemical or physical constants, are not invariable and characteristic quantities. Entirely apart from the influ-

[4a] P. Wenger and R. Duckert (*2ieme Rapport. Reactifs pour l'analyse qualitative minérale*, Basle, 1945) have suggested that the negative logarithm of the concentration be given to characterize the degree of dilution. J. Gillis [*Bull. soc. chim. France* **12**, 177 (1945)] has shown the usefulness of this value for the graphic presentation of the effect of cosolutes on the dilution limit.

ence of the other materials present, which is often extensive, these figures are always somewhat dependent on the particular volume involved and the details of the procedure employed. If, for example, a certain reaction is carried out with a solution of a given concentration (dilution) of the material to be detected, and the test is made as a spot reaction, and in volumes of 5 or 50 ml., respectively, the corresponding identification limits and concentration limits will be different in each of the 3 cases. The figures that are valid for a given volume will, as a rule, furnish only an approximate orientation for the values of the identification limit and concentration limit in volumes that are much larger or considerably smaller. Accordingly, it is not legitimate to calculate these figures for other volumes from data that have been experimentally obtained in some particular volume. An actual verification alone can give validity to such calculated values. The sensitivity of tests depends not only on the particular volumes, but also on other reaction conditions, such as the use of solid or liquid reagents, the presence of indifferent accompanying materials, temperature, *etc.* Therefore, it is never proper to state that a reaction has this or that identification concentration limit; instead, it should be stated that a given procedure furnishes this or that identification (concentration) limit of the reaction in question.

The relation between the sensitivity of a test and the volume of the test solution and the procedure employed is plainly shown by the Prussian blue reaction, which is so often used to detect iron or ferrocyanide ions. The same reaction product, a blue precipitate, is obtained by: (a) adding several milliliters of potassium ferrocyanide solution to a ferric chloride solution and filtering; by bringing together one drop of each of these solutions on (b) a spot plate or (c) on filter paper; or by (d) placing a drop of ferrocyanide solution on filter paper impregnated with ferric chloride. If the identification limit and concentration limit of this Prussian blue test are measured in each of these 4 procedures, the values are found to be quite different. The spot reaction on paper impregnated with ferric chloride gives the most favorable concentration limit for the detection of ferrocyanide, and accordingly will succeed at dilutions where the other procedures have failed. The test conditions similarly influence the quantity and concentration sensitivity of many tests. Consequently, it is always important to discover these experimental conditions, or to employ means which will lead to the maximum sensitivities of a test.

It is obviously much more difficult to detect small quantities of a reaction product obtained by precipitation or by color reactions if the volume is large than if it is possible subsequently to collect the product in a small volume. Hence, the extraction of a reaction product by a suitable solvent is frequently employed to increase the sensitivity of a test.

This is also true for accumulating a reaction product at the interface of two immiscible liquids. The observance and maintenance of definite test conditions are quite important in spot test analysis. Sometimes a reaction product can be concentrated, or the material to be detected can be localized at certain portions of the medium, if the spot reaction is carried out on paper. This localization is of fundamental importance in analysis, because without special after-treatment a local accumulation and reaction of material can never be accomplished in homogeneous solutions contained in test tubes.

The extent of the influence of the experimental conditions in spot test analysis is illustrated by the fact that even a seemingly minor matter, such as the order in which drops of the test solution and the reagent are placed on the paper, often results in distinct differences in the sensitivity of such tests. The reactivity of solids is also frequently utilized in spot tests to attain the highest possible sensitivities. This may be done in two ways. First, the solid reagent may be brought in contact with a drop of the test solution. This usually is accomplished by impregnating filter paper with the insoluble reagent, and the latter, thus finely divided, then reacts with the applied drop of the test solution. Secondly, the pulverized test material is treated directly with a solution of suitable reagents. Such topochemical reactions are discussed in detail in Chapter XI.

The reason why the identification limit and the concentration limit of a test, based on a chemical reaction, depend on the volume of the test solution and on the procedure employed is not necessarily obvious; it requires explanation. A reaction that is used for analytical purposes, because it produces slightly soluble or colored soluble compounds, is fixed by the concentration of the ion A, to be determined, remaining after AB is formed by reaction with B ions. If AB is slightly soluble, [A] is the ratio of the solubility product of AB to [B]; the latter is limited by the solubility of the reagent. If AB is soluble, the ratio of its ionization constant to [B] is the ratio between [A] and [AB]. Therefore, a slightly soluble, or a soluble colored, compound formed by an ionic reaction can be seen only if a certain ion concentration is exceeded. It might be expected, therefore, that the relation of the concentrations to the solubility (ion) product should also extend to the sensitivity, and consequently the sensitivity of a test should be greater the smaller the solubility (ion) product of the characteristic material, whose formation constitutes the basis of the test. However, experiments and studies, first made by Böttger,[5] have shown that a low value of the

[5] W. BÖTTGER, Otto Wallach Festschrift, p. 232, Göttingen, 1909; see also *Chem. Ztg.* **33**, 1003 (1909).

ence of the other materials present, which is often extensive, these figures are always somewhat dependent on the particular volume involved and the details of the procedure employed. If, for example, a certain reaction is carried out with a solution of a given concentration (dilution) of the material to be detected, and the test is made as a spot reaction, and in volumes of 5 or 50 ml., respectively, the corresponding identification limits and concentration limits will be different in each of the 3 cases. The figures that are valid for a given volume will, as a rule, furnish only an approximate orientation for the values of the identification limit and concentration limit in volumes that are much larger or considerably smaller. Accordingly, it is not legitimate to calculate these figures for other volumes from data that have been experimentally obtained in some particular volume. An actual verification alone can give validity to such calculated values. The sensitivity of tests depends not only on the particular volumes, but also on other reaction conditions, such as the use of solid or liquid reagents, the presence of indifferent accompanying materials, temperature, *etc.* Therefore, it is never proper to state that a reaction has this or that identification concentration limit; instead, it should be stated that a given procedure furnishes this or that identification (concentration) limit of the reaction in question.

The relation between the sensitivity of a test and the volume of the test solution and the procedure employed is plainly shown by the Prussian blue reaction, which is so often used to detect iron or ferrocyanide ions. The same reaction product, a blue precipitate, is obtained by: (a) adding several milliliters of potassium ferrocyanide solution to a ferric chloride solution and filtering; by bringing together one drop of each of these solutions on (b) a spot plate or (c) on filter paper; or by (d) placing a drop of ferrocyanide solution on filter paper impregnated with ferric chloride. If the identification limit and concentration limit of this Prussian blue test are measured in each of these 4 procedures, the values are found to be quite different. The spot reaction on paper impregnated with ferric chloride gives the most favorable concentration limit for the detection of ferrocyanide, and accordingly will succeed at dilutions where the other procedures have failed. The test conditions similarly influence the quantity and concentration sensitivity of many tests. Consequently, it is always important to discover these experimental conditions, or to employ means which will lead to the maximum sensitivities of a test.

It is obviously much more difficult to detect small quantities of a reaction product obtained by precipitation or by color reactions if the volume is large than if it is possible subsequently to collect the product in a small volume. Hence, the extraction of a reaction product by a suitable solvent is frequently employed to increase the sensitivity of a test.

This is also true for accumulating a reaction product at the interface of two immiscible liquids. The observance and maintenance of definite test conditions are quite important in spot test analysis. Sometimes a reaction product can be concentrated, or the material to be detected can be localized at certain portions of the medium, if the spot reaction is carried out on paper. This localization is of fundamental importance in analysis, because without special after-treatment a local accumulation and reaction of material can never be accomplished in homogeneous solutions contained in test tubes.

The extent of the influence of the experimental conditions in spot test analysis is illustrated by the fact that even a seemingly minor matter, such as the order in which drops of the test solution and the reagent are placed on the paper, often results in distinct differences in the sensitivity of such tests. The reactivity of solids is also frequently utilized in spot tests to attain the highest possible sensitivities. This may be done in two ways. First, the solid reagent may be brought in contact with a drop of the test solution. This usually is accomplished by impregnating filter paper with the insoluble reagent, and the latter, thus finely divided, then reacts with the applied drop of the test solution. Secondly, the pulverized test material is treated directly with a solution of suitable reagents. Such topochemical reactions are discussed in detail in Chapter XI.

The reason why the identification limit and the concentration limit of a test, based on a chemical reaction, depend on the volume of the test solution and on the procedure employed is not necessarily obvious; it requires explanation. A reaction that is used for analytical purposes, because it produces slightly soluble or colored soluble compounds, is fixed by the concentration of the ion A, to be determined, remaining after AB is formed by reaction with B ions. If AB is slightly soluble, [A] is the ratio of the solubility product of AB to [B]; the latter is limited by the solubility of the reagent. If AB is soluble, the ratio of its ionization constant to [B] is the ratio between [A] and [AB]. Therefore, a slightly soluble, or a soluble colored, compound formed by an ionic reaction can be seen only if a certain ion concentration is exceeded. It might be expected, therefore, that the relation of the concentrations to the solubility (ion) product should also extend to the sensitivity, and consequently the sensitivity of a test should be greater the smaller the solubility (ion) product of the characteristic material, whose formation constitutes the basis of the test. However, experiments and studies, first made by Böttger,[5] have shown that a low value of the

[5] W. BÖTTGER, Otto Wallach Festschrift, p. 232, Göttingen, 1909; see also *Chem. Ztg.* **33**, 1003 (1909).

solubility (ion) product is by no means the only factor involved. Precipitation reactions are known which prove that compounds with approximately equal solubilities can be detected with different degrees of sensitivity, but, in addition, cases can be cited in which more soluble compounds are easier to detect than others whose solubility is less. For instance, lead can be detected more easily than cadmium by precipitation as the sulfide, even though the two sulfides have practically the same solubility. Manganous sulfide is more soluble than zinc sulfide, but the precipitation of the former can be detected more readily. Still more striking is the fact that it is easier to detect the formation of lead sulfide than of mercuric sulfide, despite the fact that the latter, with its extremely low solubility product, is by far the least soluble of all sulfides. The identification limit of a colored material depends less on the smallness of the particular ion product than on the rapid development and discernibility of a color change. At equal ion products, blues or reds are more easily perceived than yellows or browns.

It must be remembered, with respect to all precipitation reactions, that if the precipitate is to be visible, much more material may have to be thrown down than is necessary merely to exceed a given solubility. There is an apparent contradiction in the fact that a more soluble compound, produced by a chemical reaction, may be easier to detect than a product whose solubility is lower, and that the ion product is not the sole determinant for the sensitivity of a reaction producing a soluble colored material. The reason for this anomaly is the existence of definite threshold values of particle size and color intensity. These values, which must be reached before a material can be perceived by the human eye, can be stated numerically. They are not directly or solely dependent on the slight solubility of a compound, but depend on additional factors. In precipitation reactions the rate of formation of the precipitate plays an especially important role. The significance of this factor becomes clear if it is remembered that the formal stoichiometric equation representing a chemical reaction presents only the "chemical fate" of the ions or molecules of the solution. The complete picture must include the subsequent aggregation of the individual molecules into larger groups. These, in turn, go through colloidal states of dispersion, overcome supersaturation conditions, and prevail over the obstructive influences of the cosolutes on these transformations. The development of a new phase, which is characteristic of a precipitation reaction, is more difficult to detect when colorless, and particularly amorphous, compounds are thrown down than when the precipitate is colored. Consequently, from the standpoint of the analytical chemist, the formation of colored reaction products, particularly precipitates, is especially interesting and desirable.

An instructive demonstration of the significance of color in improving the visibility of a precipitate is furnished by magnesium hydroxide. If the identification limit and concentration limit of the precipitation of $Mg(OH)_2$ by means of an alkali are measured for any method of carrying out this reaction—in a test tube or on a spot plate, for instance—the sensitivity will be found to be quite low because small quantities of the colorless precipitate are difficult to see. However, if the precipitation is made in the presence of certain dyes (*e.g.*, *p*-nitrobenzeneazo-α-naphthol) the dye is absorbed on the $Mg(OH)_2$, and even minute quantities, normally not visible, thus become plainly evident.[6] The effect is so great that the identification limit and the concentration limit of the pure and the absorptively tinted precipitate of magnesium hydroxide differ by powers of ten. This improvement of the test is entirely due to the increased visibility of the colored $Mg(OH)_2$ and not to the formation of a less soluble adsorption compound with a lower solubility product. This is proved by the fact that no magnesium can be detected by the aid of dye in the alkaline filtrate from a $Mg(OH)_2$ precipitation.

Further examples of raising the visibility of a reaction are: (a) traces of iron sulfide, which of themselves give only a pale green coloration, color a white aluminum hydroxide or zinc sulfide precipitate intensely gray-green or brown, respectively; (b) yellow cadmium sulfide is made dirty brown-green by even slight quantities of coprecipitated copper sulfide. Consequently, the sensitivity of a test should not lead to the conclusion that it necessarily involves reaction products with specially low solubilities (or minute ion products). This is clearly shown in the exceptionally sensitive test for silver by means of *p*-dimethylaminobenzylidene-rhodanine (page 328). This reagent produces a red precipitate and will effectively reveal silver in solutions that give a barely visible turbidity with potassium iodide. Here again, the advantage is secured not by the formation of a silver salt of decidedly lower solubility, but merely because of the increase in visibility brought about by the high molecular weight of the reagent or its reaction product. This reaction is, therefore, a very useful aid for practical purposes, particularly for spot reactions. It also demonstrates that the utilization of organic reagents to attain better visibility of reaction products deserves every consideration.

As a rule, sensitivity determinations are made by testing a given analytical reaction against increasingly dilute solutions.[7] The progres-

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[6] F. FEIGL, Experiments with K. Weisselberg, *Dissertation*, Vienna, 1930.

[7] H. FRITZ [*Z. anal. Chem.* **78,** 418 (1929)] described a very original procedure for determining the sensitivity of color reactions. It consists, essentially, in using the metal to be studied as the positive electrode, and thus bringing it anodically into solution and reaction. The cathode is a rotating cylinder on which a sheet of paper

sive repetition of such experiments invariably leads to a dilution range in which, under apparently identical conditions, the test sometimes succeeds and sometimes fails. Emich[8] has very appropriately called this the "region of uncertain reaction." For example, Richter[9] always obtained the characteristic crystals, on forty repetitions of the precipitation of magnesium by means of sodium ammonium phosphate from 40 mm.[3] of 0.05% magnesium solution, employing an equal volume of a phosphate solution of the same concentration. If solutions 10 times as dilute were used, the result was positive in only 24 attempts; with 0.001% solution, the reaction was definitely observed in only 6 instances; on further dilution to twice the volume the reaction failed completely. Probably every test has a region of uncertain reaction.[10] The considerable deviation in the statements given by even trustworthy workers as to the sensitivity of reactions is often due to the fact that such findings come from the region of uncertain reaction. Consequently, it is most urgent that experiments directed toward the determination of sensitivities be repeated sufficiently often, and that only those values be accepted in which a thoroughly unbiased observer also confirms the positive result of a reaction.

If sensitive reactions are used for tests, large quantities of the sample or test solution are not essential. The technic of spot analysis makes extensive use of this fundamental advantage. Although, as a rule, one drop of the test solution (*ca.* 0.05 ml.) is sufficient for spot reactions, it is frequently possible to attain detection limits, and, in fact, often exceed those otherwise reached only by the classic methods of microanalysis. *In consideration of the desired goal, it is, therefore, doubtless legitimate to judge the microchemical utility of a reaction solely by its identification limit,* and to use a minimum numerical value of the detection limit as a criterion for a microchemical test. It is natural to establish 10γ as this limiting value, since this is the weight that is just beyond the limit of the macro-analytical balance. In the statements of the identification limits of the spot tests, values less than 10γ will mostly be encountered, and conse-

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impregnated with the particular reagent is stretched. An electron tube furnishes the requisite constant electrolyzing current that can be quite closely regulated. The quantity of metal entering solution is fixed by the current strength and the speed of the paper (rotation rate of the cylinder), so that it is possible at all times to work quantitatively, but with avoidance of the tedious operations of weighing, dissolving, measuring, *etc.*

[8] F. EMICH, *Ber.* **43**, 10 (1910).

[9] O. RICHTER, Sitzber. Akad. Wiss. Wien, Math. naturw. Klasse, III (1902).

[10] The author has found that the region of uncertain reaction is especially observed in crystalline precipitations; it is less apparent in the formation of precipitates in spot reactions, and least in color reactions. Occasionally, a very definite reaction that can be observed at certain concentrations fails at slightly greater dilution. In such cases, the "region of uncertain reaction" is very narrow.

quently there is justification for designating such tests as microchemical. There can scarcely be any objection to freeing these tests from adherence to a given procedure since the sole object of microanalysis is to provide the possibility of detecting and determining absolutely and relatively small quantities of materials.

It is easy to decide when tests that are quantity sensitive should be used for microanalytical purposes or when those that are concentration sensitive should be employed. The former type, precipitation of crystals, for instance, is advantageous when only a small quantity of sample is available, and if there are urgent reasons for employing micro manipulations. Typical cases are the detection of possible inclusions and inhomogeneities in technical products, minerals, and so forth. Tests that are concentration sensitive are particularly necessary, and sometimes are actually indispensable, if the analytical problem is to detect traces of certain materials at high dilutions, or in association with large amounts of other materials. These conditions are often encountered in the important tasks of determining the purity of materials and of testing biological specimens. Emich[11] has aptly designated this branch of analytical practice "the search for traces" or "trace detection." The designation "trace analysis" can also be used.[12] In general, the main emphasis will be on concentration sensitive tests. They alone make it possible to apply successfully spot reactions or even test tube reactions at the high dilutions prevailing when minimal quantities of the specimen are put into solution.

As long as there was no compelling need, the detection of minimal quantities in the presence of other materials may have been considered a kind of chemical artistry; such ideas are now a thing of the past. The rapid detection of extremely small quantities of certain elements or compounds is frequently of great importance, because these may often exert an extensive influence on the behavior and the properties of industrial materials. As to the final effect, it makes no difference whether it is a question of deliberate or accidental additions, that is, of admixtures or impurities. The effect of small quantities of material is not only of

[11] F. EMICH, Lehrbuch der Mikrochemie, 2nd ed., p. 5, Munich, 1926. See also his Microchemical Laboratory Manual, translated by F. Schneider, p. 3, New York, 1932.

[12] There is as yet no general agreement on the quantity of material that constitutes a "trace." E. B. Sandell, in his excellent book, Colorimetric Determination of Traces of Metals, Interscience Press, New York, 1944, uses the term microconstituent or trace for quantities of 0.01 % or less. The author believes it would be better to define the upper limit of a trace as 10γ in unit weight or unit volume, i.e., 0.001 %. This, in qualitative trace analysis, which, of course, has to solve microchemical problems, would correspond to the maximum value of the identification limit of a microtest.

importance in industrial materials[18] but also is of great significance in the realm of Nature. Minimal quantities of materials often play a more important role in the organic substrate of vegetable or animal cells than do numerous materials which, because of their presence in large quantity, can be detected easily.

Meyer,[14] in a study of oligodynamic dilution, very appropriately remarks that a practical activity can be expected only above a certain quantity of material for a certain dilution, if it is assumed that the action originates in molecules or ions. Thus, Tammann and Rienäcker[16] found the concentration 1×10^{-9} to be the outer limit at which silver ions acts on bacteria; according to Bertrand[16] manganese salts (that seem to catalyze certain oxidation processes in the organism) act on cultures of *aspergillus niger* at a concentration of 1×10^{-10}; Schlossmann,[17] found adrenaline solutions exhibit a biological activity even at a dilution of $1:10^{18}$. These are all exceedingly small quantities of material, but nevertheless the number of molecules involved is very large[18] since 6.06×10^{23} molecules are contained in one gram molecule of a substance. Consequently, calculation showed that the most sensitive chemical reaction then known, namely, the catalytic acceleration of the reaction between silver and ferrous salts by gold salts, which permits the detection of $2 \times 10^{-7}\gamma$ Au in 2 ml.,[19] still corresponds to 300 million gold molecules. Likewise, the identification limits of the most sensitive spot reaction, and also of all chemical reactions, give exceedingly large figures if the detectable quantities of materials are recalculated in terms of numbers of molecules.

Sensitive reactions are not only of the highest importance in the search for traces (for instance, tests of purity); they may also render valuable service in the course of the systematic analysis of mixtures whose components show no extreme differences in quantity. Attention is directed to the fact that the necessary separations, which are a part of all system-

[13] In this connection, see the interesting paper by J. Alexander, *The Importance of Impurities* [*Ind. Eng. Chem.* **16**, 190 (1923)], which lists helpful and troublesome traces in different materials. References concerning metals and alloys are given by C. Smithells and W. Hessenbruch, Beimengungen und Verunreinigungen in Metallen, p. 139 ff., Berlin, 1931.

[14] J. MEYER, *Chem. Ztg.* **55**, 85 (1931).

[15] G. TAMMANN and W. RIENÄCKER, *Z. anorg. allgem. Chem.* **170**, 288 (1928); *cf.* also P. ANDRESEN, *Chem. Abstracts* **22**, 3190 (1928) and H. FROMHERZ and J. HEISS, *Z. angew. Chem.* **50**, 679 (1937). L. A. GOETZ and S. GOETZ, *Phys. Rev.* **59**, 219 (1947).

[16] G. BERTRAND, *Z. angew. Chem.* **44**, 521 (1931).

[17] H. SCHLOSSMANN, *Arch. exptl. Path. Pharmakol*, **121**, 160 (1927).

[18] Compare M. NEISSER and F. EICHBAUM, *Ergeb. Hyg. Bakt. Immunitätsforsch. exptl. Therap.* **3**, 170 (1932).

[19] P. KRUMHOLZ and H. WATZEK, *Mikrochim. Acta* **2**, 80 (1937).

atic qualitative procedures, are often accompanied by considerable losses of the constituents because of absorption, induced precipitations, *etc.* If more sensitive reactions are utilized, all the constituents of a mixture can be detected at their proper places in the analytical scheme, despite losses which are of considerable consequence when dealing with slight quantities of material.

There are cases in which there is no real necessity for using very sensitive reactions. This is by no means a justification for regarding a possible "supersensitivity" of a test as a disadvantage, because, if excessive sensitivity must be guarded against, other less delicate reactions, of which there is no lack, can be used. The possibility of making a choice and the intelligent application of reactions of different sensitivities are of particular value to the experienced analyst. He will then occasionally be in a position to draw conclusions as to the distribution of the quantities present in mixtures by studying the results of reactions of varying sensitivities applied to equal volumes of the solution.

Although there is no adequate reason for hesitating to use supersensitive reactions, every consideration should nevertheless be given to the doubt as to whether it is at all possible to detect, by purely chemical methods, such small quantities of material as are of importance, for instance, in biologic morphologic, and metabolic problems. In a very remarkable study, Brunswik,[20] on the basis of mathematical considerations, concluded that the microchemical methodology then available could not contribute decisively to the solution of such problems, because of too low sensitivity and of too little subtile localization. Liesegang,[21] and likewise Mayrhofer,[22] came to similar decisions. The author does not agree with the views of these workers regarding the sensitivity of tests for inorganic materials. A considerable number of very delicate tests using organic reagents are now known, and there is every likelihood that the sensitivity of such aids will be raised by altering their structure (*e.g.*, by introduction of other atomic groups). But above all, as the author has pointed out on several occasions,[23] a fact that has now been observed seems to be of great significance for the development of highly sensitive tests: namely, the analytical utilization of induced and catalyzed reactions in which such effects serve to reveal the inductor or the catalyst. It is possible to detect exceedingly small quantities in this way. Such tests are discussed in Chapter V.

[20] H. BRUNSWIK, *Naturwissenschaften* 11, 881 (1923).

[21] R. LIESEGANG, *Z. wiss. Mikroskop.* 41, 25 (1924).

[22] A. MAYRHOFER, *Mikrochemie* 3, 68 (1925).

[23] F. FEIGL, *Z. angew. Chem.* 44, 739 (1931); F. FEIGL and E. FRÄNKEL, *Ber.* 65, 539 (1927).

No matter how great the significance of the sensitivity of a reaction may be for its analytical evaluation, it is not permissible to appraise a test on the basis of sensitivity alone. This is particularly true because, in almost all practical cases, it is but seldom possible to depend on a single material being present in a state of complete purity. Consequently, there is frequent need for reactions whose activity is limited to the smallest possible number of materials. According to a decision of the International Commission on New Analytical Reactions and Reagents,[24] **specific** and **selective** reactions (reagents) are to be differentiated. Reactions (reagents) which, *under definite experimental conditions*, are quite unambiguous for one component, are termed **specific**; on the other hand, those reactions (reagents) which permit a narrow choice, because they are characteristic for a limited number of ions or components, are termed **selective.** Accordingly, there are reactions (reagents) that are more or less selective. On the other hand, a reaction (reagent) is either specific or non-specific. There are now available numerous tests which, either alone or under properly chosen experimental conditions (*e.g.* masking), can be termed selective. In contrast, the number of really specific tests (special reactions and special reagents) is still quite small. This applies especially to qualitative inorganic analysis, and even more so to qualitative organic analysis.

The methodology of chemical analysis must take this condition into account. It does so, in the detection of the ingredients of a mixture, by separating certain materials into groups, followed by separate examination of the group precipitates. The course of the systematic analysis, entirely apart from the unavoidable losses involved, thus becomes tedious and time consuming. Consequently, specific reactions possess considerable analytical importance, because with their aid it is often possible to simplify appreciably the analytical procedure. All efforts in this direction deserve special consideration. The simplification of analytical methods through the use of tests that are more sensitive and more selective is particularly striking in the technical examination of materials, in identification of rocks, and in testing the purity of materials.

The discovery of specific or selective reagents is still largely empirical, but certain guides may be indicated. All previous experience makes it certain that specific or selective reagents for inorganic analysis should be sought among organic compounds, which, because of their variety, afford a far from exhausted reservoir of possible reagents. This search, however, is not limited entirely to hit or miss trials because, in all likeli-

[24] Compare *Mikrochim. Acta* 1, 253 (1937). See also Tables of Reagents for Inorganic Analysis. First Report of the International Committee on New Analytical Reactions and Reagents of the Union internationale de chimie, Leipzig, 1938.

hood, the specific (selective) action of organic compounds is always concomitant with the presence of certain groups of atoms. With a knowledge of such group actions in a certain compound it is then often possible, by a more or less extensive alteration of the molecule (introduction of other groups that increase the weight or solubility or produce color) to raise the analytical value of the original compound, or to bring other compounds which have a group known to be specific or selective into the range of the investigations. The possibility of improving a reagent by this preparative method is doubtless a very desirable advance. Characteristic examples of this will be given in Chapters VI and VII. The knowledge and use of group actions in organic compounds is also of great importance in qualitative organic analysis, when the principal task is to reveal with certainty the presence of certain groups (compare Chapter VIII). Possibilities of particularly indubitable tests may be expected among the catalyzed reactions, because the essence of the activity of catalysts is that they not only act in small quantities, but also specifically. The same is largely true for the so-called "induced" reactions (see Chapter V).

Selective or even specific reactions with reagents that ordinarily are nonselective are occasionally available. This is the case when it is possible to inactivate the attendant materials that would give similar reactions. Many examples show that even a nonspecific reagent can, by suitable precautions, be made to undergo a desirable limitation of its activity. For instance, thiocyanates react in acid solution with ferric and cobalt salts to form soluble red and blue double thiocyanates, respectively. Consequently, the sensitive test for cobalt by means of thiocyanate cannot be applied in the presence of ferric ions. However, the addition of alkali fluoride[25] or syrupy phosphoric acid[26] so greatly decreases the concentration of the ferric ion, by the formation of complex ions, that the ion concentration requisite for the formation of ferric thiocyanate is not reached, and the interference by iron is thus completely eliminated.

The preceding example of *masking* is of basic significance. Such maskings, which are applicable in many other cases, provide a means of producing, to a certain extent, a suitable reaction environment in which, then, even a nonspecific reagent can exhibit unequivocal action. The use of masking agents is no longer a matter of accident, because a methodical choice of suitable masking agents can now be made on a basis of the present intimate knowledge of complex types of compounds. The inverse of masking, namely the process of *demasking*, should be mentioned here. It likewise can be made the basis of tests that are more selective

[25] I. KOLTHOFF, *Mikrochemie* 8, 176 (1930).
[26] Unpublished results of L. Melnik.

and sensitive. These topics will be treated again in the discussion of pertinent examples, and also in connection with the practical application of reaction masking and demasking in Chapter IV. Only a preliminary comment is included here, namely, that spot reactions on paper occasionally give unequivocal tests with unspecific reagents even without masking agents, because capillary separation of the components of the solution sometimes produces separate zones on the paper. These localizations permit the recognition of compounds in the presence of each other with the same reagent.[27] This will be discussed in more detail in Chapter X.

It is obvious that reagents which react simultaneously with two or more materials either cannot give unequivocal tests, or they do so only under special conditions. Likewise, color reactions in solutions which are themselves colored, and colored precipitates that are enveloped by other precipitates, often cannot be detected. Less apparent, however, is the fact that materials, which seemingly are quite indifferent, can often decrease the sensitivity of a test, even to a considerable degree. For instance, the addition of a solution of the sodium salt of the osazone of dihydroxytartaric acid to warm, very dilute, neutral calcium solutions, results immediately in a dense precipitate of the calcium salt; magnesium salts do not react at all under these conditions. Nevertheless, this sensitive test for calcium (identification limit 6γ Ca in 3 ml.) is useless in the presence of even ten times the quantity of magnesium, because no precipitate appears then.[28] A similar phenomenon occurs in the reaction between 1, 3-dihydroxyanthraquinone and calcium salts. The sensitivity is greatly decreased in the presence of barium salts which by themselves do not react.[29]

More or less extensive lessening of sensitivities are encountered in practically all tests because of the presence of materials which of themselves do not react with the particular reagent. In reality, infallibility of a test is extremely rare, and certainty is attained only within particular limits of concentration of the accompanying materials. The nature of these materials obviously is of great importance. Consequently, it is always necessary to test the behavior of a reaction that is accepted as specific or selective on as many mixtures as possible to avoid unpleasant surprises. The impairment of tests frequently does not become apparent until high dilutions are reached; indifferent materials not only lower the sensitivity to various degrees, but they also usually extend the region of

[27] F. FEIGL, Spot Tests, p. 59.
[28] According to experiments by S. Pickholz. Compare F. FEIGL, Spot Tests, p. 170.
[29] P. KRUMHOLZ, unpublished studies.

"uncertain reaction." This circumstance is a further reason for the necessity of highly sensitive reactions, since their detection limits, even after some increase, still frequently remain sufficiently low to meet given demands.

Probably various factors are active in the lowering of sensitivity by indifferent materials. In precipitation reactions a lag in the aggregation of the particles may play an important part as was first indicated by the studies of Pickardt.[30] He found that foreign materials can cause a lowering of the crystallization velocity proportional to the square root of the concentration of the foreign material. Phenomena pertinent to these effects will be discussed in Chapter XI in connection with the genetic formation of materials. Because of the possibility of such influences, the characterization of a reaction, according to sensitivity and infallibility, should always be supplemented by a statement of possible limitations of its sensitivity due to the other materials present. In his papers on the microchemical analysis of mixtures, Schoorl[31] was the first to call attention to the effect of indifferent attendant materials. He took account of their quantity in his determinations of sensitivity and coined the term **"limiting proportion"** for the ratio of the quantity of material that could just be detected to that of the attendant material. A knowledge of these limiting proportions is of particular importance for practical purposes, and the publication of as many such data as possible would doubtless help to meet a pressing need. Furthermore, determinations of the limiting proportion would be of value for another reason, namely, that the sensitivity of a test is sometimes raised by "indifferent" materials. Thus Kolthoff[32] showed that the detection of magnesium by means of titan yellow is considerably more delicate in the presence of calcium salts, which of themselves do not react with this reagent. Similar phenomena will be discussed in the consideration of induced reactions and their analytical uses (Chapter IV).

The field of application of analytical tests is practically never constant, because of the continuously changing experimental conditions. Many different demands must be met in the solution of analytical problems, and consequently a biased preference for certain methods of detection must be condemned. The suitable choice of reactions is conditioned by sensitivity (detection limit, concentration limit), certainty, and limiting proportion. Data on these characteristics establish all the advantages and disadvantages of chemical methods of detection, and

[30] V. PICKARDT, Z. physik. Chem. **42,** 17 (1900).

[31] N. SCHOORL, Z. anal. Chem. **46,** 658 (1907).

[32] I. KOLTHOFF, Chem. Weekblad **24,** 254 (1927).

allow a recognition of the needs posed by analytical problems, whose solution requires further study.[33]   Complex chemistry plays a dominant role in all such research, which must primarily take account of sensitivity and selectivity.   Consequently, a knowledge of the fundamental facts of the chemistry of the complex compounds is of the highest importance for the theory and practice of analytical chemistry.   Chapter III will deal with this topic.

[33] Compare F. HAHN, *Z. angew. Chem.* **44**, 456 (1931).

CHAPTER III

Types of Complex and Coordination Compounds Which Play a Role as Reactants and Products of Reaction in Analytical Processes

Many compounds can be regarded formally as combinations of molecules that ordinarily are perfectly capable of stable independent existence. For instance, the molecule of $Fe(CN)_2$ can combine with four molecules of KCN to form the stable compound $K_4Fe(CN)_6$, whose properties are completely different from those of its components, and which, in aqueous solution, dissociates into K^+ and $Fe(CN)_6^{----}$ ions. Such compounds are called auxiliary valence or complex compounds. Attempts to formulate them by joining the principal valences of the atoms fail if the ordinary valences of the atoms in the compounds are retained. It is necessary, rather, to assume that the apparently saturated compounds still possess additional combining capacity, which finds its expression in the formation of complex compounds. Such combining capacities are called auxiliary valences or covalences.

Although the actual nature of auxiliary valences is not known, the coordination theory proposed by Alfred Werner in 1893 provides an excellent systematization of the complex compounds. It is based essentially on stereochemical considerations.

Inorganic complex compounds, according to this theory, consist of a *central atom* around which are grouped (*coordinated*) a number of *ligands* (*i.e.*, attached atoms or groups). Their number, the *coordination number*, is determined primarily by spatial considerations; it is usually 6, 4, 3, or 2. Potassium ferrocyanide, $K_4Fe(CN)_6$, is thus interpreted:

$$K_4 \begin{bmatrix} CN\cdot & \cdot CN \\ CN\cdot Fe\cdot CN \\ CN\cdot & \cdot CN \end{bmatrix}$$
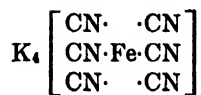
The CN groups in the "first sphere" are arranged octahedrally around the central Fe^{II} atom, and are bound to it by *nonionogenic* auxiliary valences that are absolutely equivalent to each other. In contrast, the K^+ ions in the "second sphere" are bound *ionogenically* to the $Fe(CN)_6^{----}$ group by normal polar principal valences.

The surpassing service of the Werner method of writing complex compounds lies not only in the fact that it reproduces accurately the steric structure of the solid compounds, but also in furnishing correct predictions of the behavior of these compounds in aqueous solution. Thus, the foregoing representation of $K_4Fe(CN)_6$ shows clearly that the molecule dissociates into $Fe(CN)_6^{----}$ and four K^+ ions, while the bond

23

between Fe^{++} and CN^- is complex, and therefore nonionogenic. The $Fe(CN)_6^{----}$ undergoes a secondary dissociation into Fe^{++} and six CN^-, but only to an extremely small extent. Other complex ions, such as $Cd(CN)_4^{--}$, dissociate to a much greater degree (into Cd^{++} and CN^-). The degree of the complex character of an ion is best expressed by the complex constant
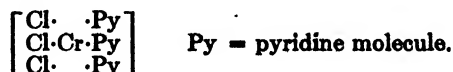
$$K_{complex} = \frac{[\text{complex ion}]}{[\text{component I}] \cdot [\text{component II}]}$$

The complex constant gives a measure of the stability of complex compounds, and the foregoing equation, which is only a special formulation of the general law of mass action, shows that the concentration of a complex ion in solution can be increased by raising the concentration of one or more of the components.

Analytical chemistry has received many fruitful suggestions from the coordination theory because the possibility of using reactions that lead to complex compounds is closely related to the problems of certainty and sensitivity. The conversion of one species of ion into another affords the extraordinarily significant possibility of diminishing the concentration of an ionic species, and this may proceed so far that even sensitive reactions that require only a small ion product can no longer occur. This process is known as *reaction masking* and will be discussed in greater detail in Chapter IV. It will suffice here to point out the general fact that complex compounds differ considerably from their components in their chemical and physical properties. Even unstable compounds, or those which cannot exist independently (*e.g.*, those of metals with anomalous valences), can be stabilized, often to a surprising degree, by complex formation. An acquaintance with the fundamentals of the chemistry of the complex compounds is, therefore, of equal importance to the theory and practice of analytical chemistry. Only the more important types will be discussed here.

Inorganic complex compounds, on the basis of the Werner system, can be classified as of three main types: *addition compounds, intercalation or penetration compounds, and inner complex compounds.*

A typical example of the first type is $CrCl_3 \cdot 3Py$. In aqueous solution this compound is not an electrolyte, a fact that is expressed by the coordination formula:

$$\begin{bmatrix} Cl \cdot & \cdot Py \\ Cl \cdot Cr \cdot Py \\ Cl \cdot & \cdot Py \end{bmatrix} \quad Py = \text{pyridine molecule.}$$

Consequently, the nature of addition compounds is such that the bond between the central atom (Cr) and the anionic constituent (Cl) is not broken, but rather is so greatly stabilized by the entrance of further

ligands that it becomes nonionogenic. However, this is not true of all complex salts of this kind, since numerous addition compounds exhibit electrolytic properties. This always is the case if an ion complex rather than a "neutral component," such as ·Py or NH_3, is added. Thus $Co(NO_2)_3 \cdot 3KNO_2 = K_3[Co(NO_2)_6]$ is a typical addition compound since the Co—(NO_2) bond originally present is not broken.

The term *intercalation or penetration compound* is derived from the fact that the ligands enter between the anionic constituent and the cationic constituent—functioning as the central atom—and thus loosen the bond between anion and cation. An example is tetramminocupric sulfate

$$CuSO_4 \cdot 4NH_3 = \begin{bmatrix} NH_3 \cdot & \cdot NH_3 \\ & Cu \\ NH_3 \cdot & \cdot NH_3 \end{bmatrix}^{++} SO_4^{--}$$
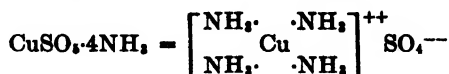
in which only the NH_3 molecules, but not the SO_4^{--} ion, are bound to the copper ion by auxiliary valences.

In certain complex compounds, ring systems are formed through the action of auxiliary valences. Usually organic compounds of higher molecular weights are the attached groups in these materials. Thus ethylenediamine, $H_2N(CH_2)_2NH_2$, forms complex ions with numerous metallic ions, cadmium, for instance:

$$\begin{bmatrix} & H_2 & & H_2 & \\ H_2C—N & & N—CH_2 \\ & & Cd & & \\ H_2C—N & & N—CH_2 \\ & H_2 & & H_2 & \end{bmatrix}^{++}$$
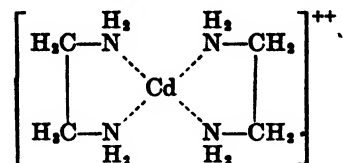
The Cd^{++} ion is thus bound complexly to the two NH_2 groups of each diamine molecule, with formation of stable, five-membered rings. Consequently, one molecule of the diamine occupies two *"coordination positions."* According to Pfeiffer[1] such complex compounds, in which rings are formed by the complex binding of an ion at two places on a molecule, are called *auxiliary valence rings of the second kind.* If the ring includes several metal atoms, as for instance,

$$\begin{array}{c} H \\ O \\ Fe \qquad Fe \\ O \\ H \end{array}$$
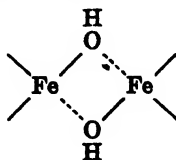
an *auxiliary valence ring of the third kind* is present.

[1] P. Pfeiffer in K. Freudenberg's Stereochemie, p. 1356. Leipzig and Vienna, 1933.

Finally, there are compounds in which a metal atom is bound both by salt-like and complex bonds to different parts of a molecule.   A case in point is the copper salt of glycine

$$
\begin{array}{ccccc}
 & \overset{\text{H}_2}{\text{N}} & & \text{O}-\text{C}{=}\text{O} \\
\text{H}_2\text{C}-\text{N} & & \text{Cu} & \\
 & \text{O}{=}\text{C}-\text{O} & & \text{N}-\text{CH}_2 \\
 & & & \underset{\text{H}_2}{}
\end{array}
$$
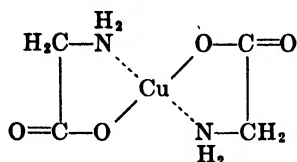
The complex nature of this compound is shown by the fact that it is a non-electrolyte.   These materials, which are especially important in analytical chemistry, are known as *inner complex compounds*, according to Ley,[2] or, following Pfeiffer's proposal, as *auxiliary valence rings of the first kind.*

There also exist water-soluble ionogenic complex compounds, whose anions consist of ring systems formed by the action of principal and auxiliary valences of a metal atom directed toward atoms of an organic acid radical.   These are known as inner complex anions.   Instances are also known in which water-insoluble inner complex salts are soluble in strong alkalies, with formation of inner complex anions.

A special class of complex compounds, that formally are to be regarded as addition compounds, are the molecular compounds consisting entirely of organic components.   In them, the molecular ratio of the components is frequently 1:1 or 1:2.

In the following discussion, first place is given to types of complex compounds of which representatives have been isolated in solid, often crystalline form, and whose composition, when they are soluble in water, has often been confirmed by conductance measurements.   Such stoichiometrically defined compounds can be classified according to their linkage scheme, without regard to the particular nature of the compounds of the complex.   The great majority of complex compounds that play a role in analytical chemistry as reagents, as reaction products, or as intermediates preceding analytical operations, belong to stoichiometrically defined types.

In a wider sense, complex compounds also include the products of the union of molecules of various materials in which the molecular ratios are not maintained at á particular value.   Complex compounds of this kind, as well as others to which no stoichiometrically defined composition can be assigned because the materials have not been isolated, may also have analytical importance.   The formation of such compounds has

[2] H. LEY, *J. Elektrochem.* **10**, 954 (1904).   Concerning the theory of inner complex salts, see P. KARRER and coworkers, *Helv. Chim. Acta* **2**, 292 (1919).

still greater significance with respect to the process of solution, the colloidal condition, for absorption processes, and for the occurrence of certain catalyzed reactions. Complex compounds that are not stoichiometrically defined will be discussed on page 60 of this chapter, and at numerous other places in the text.

The compounds discussed below are representatives of the several thousand complex compounds that have been isolated, and that can be classified on the basis of their structures as symbolized by their coordination formulas. It has been found that complex compounds play an important part in all fields of inorganic and organic experimental chemistry, in mineral and physiological chemistry, and in the applications of chemistry in the industries. Regarding analytical chemistry in particular, it can be definitely asserted that the introduction of ideas on complex compounds and chemical coordination have had and will continue to have at least as permanent and important an effect on the theory and practice of chemical analysis as the ionic theory. Consequently, in all parts of this book, which deals primarily with the problems of the specificity, selectivity and sensitivity of tests, stress will be laid on ideas and considerations based on the coordination theory.

An advance of general chemical significance that has come from complex chemistry is the preparation it has provided for new concepts of and researches on chemical binding forces. Werner, who himself isolated many coordinated compounds and experimentally established their consititution, was the first to state clearly that chemical binding powers are still resident in compounds which are ordinarily viewed as saturated. This idea of residual valence is now accepted universally. His outstanding successes inspired an enormous number of investigations on the isolation of complex compounds which, quite apart from other applications, now provide the material for studies of the molecular and atomic physical requirements for the existence of complex compounds. It is beyond the scope of this book to deal in detail with the related problems and studies that, for the most part, are more physical than chemical. It should be noted, however, that every variety of chemical binding between atoms and molecules is now ascribed eventually to a mutual action of electric charges resident within the atoms and molecules. Within this framework complex compounds doubtless exhibit different types of mutual actions related to the molecular structure of the components. This is particularly indicated by the observations that there are gradations in stabilities and tendencies toward formation of complex compounds, ranging from quite loose combinations to a stability fully equal to that of compounds produced by the action of principal valence forces.

The following [books should be consulted for a more extensive study of the chemistry of complexes:

A. WERNER, *New Ideas on Inorganic Chemistry.* 2d ed. Translated by E. Hedley. New York, 1911. 4th German ed. 1921.

A. WERNER and P. PFEIFFER, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie,* 5th ed. Brunswick, 1923.

R. WEINLAND, *Einführung in die Chemie der Komplexverbindungen.* 2d ed. Stuttgart, 1924.

P. PFEIFFER. *Organische Molekülverbindungen.* 2d ed. Stuttgart, 1927.

F. DEDE, *Komplexchemie.* Sammlung Göschen, Berlin, 1928.

R. SCHWARTZ, *The Chemistry of the Inorganic Complex Compounds.* Translated by L. Bass. New York, 1923.

W. THOMAS, *Complex Salts.* London, 1924.

H. EMELÉUS and J. ANDERSON, *Modern Aspects of Inorganic Chemistry.* New York, 1938.

F. EPHRAIM, *Chemische Valenz-und Bindungslehre:* Leipzig, 1928; *Inorganic Chemistry,* 4th ed., New York, 1943.

G. BRIEGLEB, *Zwischenmolekulare Kräfte und Molekülstruktur.* Stuttgart, 1937.

L. PAULING, *The Nature of the Chemical Bond.* Ithaca, 1940.

## AMMONIA AND ITS DERIVATIVES AS CONSTITUENTS OF COMPLEX COMPOUNDS

The ammonia molecule, because of its pronounced dipole nature, possesses a great tendency to combine with metal ions and form stable complex compounds known as *ammoniates or ammine compounds.* The ammonia molecule is doubtless bound through the nitrogen atom. According to Werner, ammonium hydroxide can be considered an addition compound with reference to the ammonia molecule, and as an intercalation compound with respect to one hydrogen atom of water. The coordination of ammonia causes an increase in the original slight dissociation of the water. Formation of NH_4^+ and OH^- ions, with consequent basicity of aqueous ammonia solutions, ensues. If the ammonium ion is formulated $H \ldots NH_3^+$, either the hydrogen atom with the coordination number 1, or the nitrogen atom with the coordination number 4, may be regarded as the central atom. In either case, the stability of the ammonium ion indicates that the four hydrogen atoms in the first sphere have similar linkings, which argues for the assumption of the nitrogen as the central atom.

Many metal salts are capable of forming ammoniates containing several ammonia molecules. The solubility in ammonia of the hydroxides of silver, copper, cadmium, and zinc is due to the formation of complex intercalation compounds such as $[Ag(NH_3)_2]OH$, $[Cu(NH_3)_4](OH)_2$, or the corresponding ammine ions. Solid ammine salts of these metals, with various acid radicals, have been prepared in large numbers. Silver

chloride, in contrast to silver iodide, is easily soluble in ammonia, with formation of $Ag(NH_3)_2Cl$. Hence, a certain concentration of silver ion is necessary for complete conversion into the complex $Ag(NH_3)_2^+$ ion. This concentration, corresponding to the difference in the solubility products of AgCl and AgI, is furnished by the more soluble silver chloride, but not by silver iodide. . On the other hand, the precipitation of silver chloride from its ammoniacal solution by nitric acid, and the decolorization of the blue copper tetrammine salt solutions by acids, is due to the fact that the acidified solutions, because of formation of NH_4^+ ions, do not contain enough NH_3 molecules to form the respective complex ammine ions.

The coordination ability of ammonia is not limited to metal ions. Certain metal molecules (which, being monatomic, are identical with the metal atoms) also form compounds by uniting with ammonia molecules. Instances are $Ba(NH_3)_6$ and $Ca(NH_3)_6$, which are obtained by dissolving the metal in liquid ammonia and allowing the solution to evaporate. Such examples show, as do the metal hydroxides which are soluble in aqueous ammonia, that solubility and complex salt formation are closely allied, and that the coordination ability of certain atoms is important to this finding.

The coordination ability of the nitrogen atom is retained also in organic derivatives of ammonia. For instance, ethylenediamine, $H_2N-CH_2-CH_2-NH_2$ (= en) can form stable complex compounds, such as $Co(en)_3Cl_3$. A comparison of this compound with $Co(NH_3)_6Cl_3$, shows that one molecule of ethylenediamine is equivalent in coordination capacity to two molecules of ammonia and, accordingly, can occupy two coordination positions of the cobalt atom:

$$\left[Co\left(\begin{matrix} \overset{H_2}{N}-CH_2 \\ | \\ N-CH_2 \\ H_2 \end{matrix} \right)_3 \right] Cl_3,$$
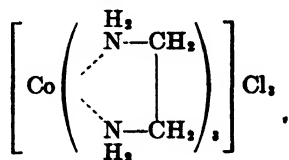
Groups which occupy two or more coordination positions are termed chelate (= a crab's claw) groups. Cyclic nitrogen bases and aromatic amines such as

pyridine , quinoline ,

benzidine H_2N- $-NH_2$, *etc.*,
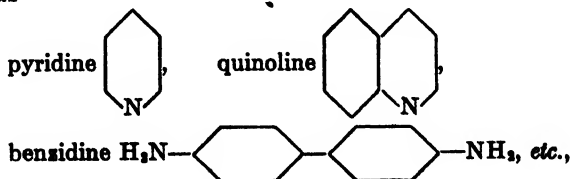
may likewise function as the neutral portions of complex compounds.

The concomitant formation of large and heavy molecules is probably the reason why so many of such compounds are only slightly soluble.

It is remarkable that the foregoing cobalt compound, and other ammine salts with ethylenediamine molecules as neutral portions, are far more stable than the corresponding ammoniates; in aqueous solution they suffer far less hydrolysis. A ring closure follows the coordination of the diamine, and in complex compounds ring formation quite generally confers greater stability. A similar ring closure, which likewise leads to an auxiliary valence ring of the second kind (see p. 25), is also present in the soluble ferrous salts of α,α'-dipyridyl ($= \alpha,\alpha'$-dip) and α,α'-phenanthroline ($= \alpha,\alpha'$-phen). The ions $[Fe(\alpha,\alpha'\text{-dip})_3]^{++}$ and $[Fe(\alpha,\alpha'\text{-phen})_3]^{++}$ are red and extraordinarily stable (see p. 319). These compounds exemplify the interesting phenomenon that auxiliary valence rings stabilize valences which the metals otherwise do not exhibit. The compounds $[AgPy_4]S_2O_8$,[3] $[Ag(\alpha,\alpha'\text{-dip})_2]S_2O_8$, and $[Ag(\alpha,\alpha'\text{-phen})_2]S_2O_8$,[4] in which silver is divalent, are known. Thallic chloride, which forms no ammoniate by the wet method, under the same conditions, and according to the quantities used, forms the following ethylenediamine compounds: $TlCl_3\cdot 3en\cdot 3H_2O$; $TlCl_3\cdot 2en\cdot H_2O$, and $TlCl_3\cdot en\cdot H_2O$.[5] Furthermore, mere addition of NH_3 or N_2H_4, respectively, results in the production of the stable $[Cu(NH_3)_4]I_2$ and $[Cr(N_2H_4)_6]Cl_2$ from the normally unstable cupric iodide and chromous chloride,[6] respectively.

Water and Its Derivatives as Constituents of Complex Compounds

The complex compounds that contain water molecules as the neutral portion are called hydrates. The coordination capacity here is likewise due to the dipole nature of the water molecule, and the auxiliary valence action is doubtless localized on the oxygen atom. The formation of hydrates is of fundamental importance for the solubility of compounds, because materials dissolved in water certainly are always hydrated (see p. 383). Water molecules may be retained as integral constituents of the space lattice of solid compounds obtained by evaporation of aqueous solutions, in so far as they are necessary for the crystal structure. Therefore, the hydrates most frequently encountered are compounds containing "water of crystallization."

Numerous hydrates can be conventionally compared to the analogous ammoniates, with respect to the number of their coordinated water

[3] G. Barbieri, *Chem. Abstracts* **6**, 3068 (1912); cf. also *Ber.* **60**, 2424 (1927).
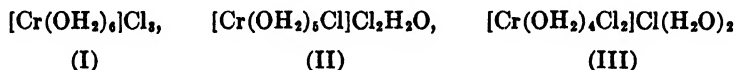
[4] W. Hieber and F. Mühlbauer, *Ber.* **61**, 2149 (1928).

[5] W. Hieber and F. Sonnekalb, *Ber.* **61**, 555 (1928).

[6] W. Traube and W. Passarge, *Ber.* **46**, 1505 (1913).

molecules. Some complex compounds contain both ammonia and water molecules as the neutral portions. • These are known as aquoammine salts. In addition, there are many hydrous compounds whose structure is far less apparent than that of the ammoniates. This is partly due to the fact that, in contrast to ammonia, the water molecule as neutral portion can be bound also in the anionic constituent of compounds.

The hydrates and aquo salts, like all other complex compounds, can be divided into distinct types which are formally expressed in the coordination formulas. Not only is a systematic principle of classification taken into account in these formulas, but the coordination formulas frequently express certain characteristics of compounds. This was pointed out with the ammoniates, and also holds for the complex compounds containing water. For instance, the hydrates of chromic chloride have the same empirical formula, $CrCl_3 \cdot 6H_2O$, but they differ essentially, not only in color, but also in their physical and chemical behavior. These differences are clearly expressed by the coordination formulas:

$$[Cr(OH_2)_6]Cl_3, \qquad [Cr(OH_2)_5Cl]Cl_2H_2O, \qquad [Cr(OH_2)_4Cl_2]Cl(H_2O)_2$$
$$\text{(I)} \qquad\qquad\qquad \text{(II)} \qquad\qquad\qquad\qquad \text{(III)}$$
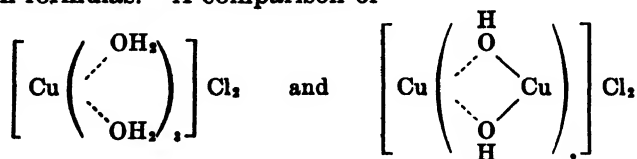
While all three chlorine atoms are bound ionogenically in (I), this is not true in the others; in (II) and (III), one or two chlorine atoms, respectively, because of coordination in the first sphere of the chromium atom, are no longer dissociable, and consequently cannot be precipitated from cold aqueous solution by silver nitrate. The water molecules in these hydrates are likewise bound differently. Only (II) and (III) lose one or two molecules of water, respectively, in a desiccator, while the water molecules in the first sphere of·all three are so firmly bound that they are not given off, no matter how long the compounds are kept over concentrated sulfuric acid. The three isomeric hydrates have different colors; (I) is violet, (II) green, (III) light green. Hence, the coordinative linkage can be of importance with respect to the color of compounds, a fact for which numerous examples can be cited from all the various types of complexes. A change in color may be brought about by the formation of a complex, and also a shift in the light absorption from the invisible to the visible part of the spectrum may occur. This finding is particularly worthy of note from an analytical standpoint.

Water molecules may be coordinated, not only on cationic but also on anionic constituents of a salt. The vitriols present pertinent examples of this. For instance, in blue vitriol, $CuSO_4 \cdot 5H_2O$, and green vitriol, $FeSO_4 \cdot 7H_2O$, the addition of water should be formulated as $[Cu(H_2O)_4]$-$[H_2O \cdot SO_4]$ and $[Fe(H_2O)_6][H_2O \cdot SO_4]$, respectively. In this connection it should be noted that *all* ions in aqueous solution are always hydrated,

even though the extent of the hydration, *i.e.*, the number of bound H_2O molecules, cannot be stated. The symbolic notations Na^+, Cl^-, H^+, *etc.*, in the strict sense, therefore, are not correct for ions in aqueous solution. They should be written $[Na(H_2O)_x]^+$, $[Cl(H_2O)_x]^-$ or $[H(H_2O)_x]^+$. Anhydrous Na^+ and Cl^- ions are present only in solid NaCl, *i.e.*, in the lattice of NaCl crystals.

The addition of water to a metal salt is capable not only of changing the dissociation relationships of the heteropolar constituent of the complex, as in the hydrates of chromic chloride (see p. 31), but, at the same time, the water molecule itself may be forced to undergo an anomalous dissociation. The conversion of water to a base in $[H \cdot NH_3]OH$ has a counterpart in $AuCl_3 \cdot H_2O$. This hydrate of auric chloride is a strong acid, and accordingly, its formula should be written $H[AuCl_3 \cdot OH]$. By coordination on the gold chloride, the water molecule has become an acid. Concentrated zinc chloride solutions act as strong acids: they change the color of indicators and disolve metals with liberation of hydrogen. Likewise boron fluoride dihydrate, $BF_3 \cdot 2H_2O$, dissolves metals, metal oxides, and carbonates.[7] These properties also are results of the acidification of water, because of the formation of complex compounds such as $[BF_3(OH)][H \cdot H_2O]$ and $H_2[ZnCl_2(OH)_2]$. Such compounds are called *hydroxoacids*. They make it probable that, in aqueous solution, H^+ ions in general are formed from water molecules as a result of addition of certain compounds. OH^- ions behave similarly.[8]

Since the additive capacity of water is localized on its oxygen atom, this property is manifested also in its inorganic and organic derivatives. Basic salts, provided they are not mixtures, can often be represented by coordination formulas. A comparison of

$$\left[Cu \left(\begin{smallmatrix} OH_2 \\ \\ OH_2 \end{smallmatrix} \right)_2 \right] Cl_2 \quad \text{and} \quad \left[Cu \left(\begin{smallmatrix} H \\ O \\ \diagdown \\ Cu \\ O \\ H \end{smallmatrix} \right)_2 \right] Cl_2$$

shows the formal relation between the hydrate and the basic salt. To cite only one example of many, the hydrate and alcoholate of calcium chloride in the coordination formulas

$$[Ca(OH_2)_6]Cl_2 \quad \text{and} \quad [Ca(C_2H_5OH)_6]Cl_2$$

[7] In this connection, compare the extensive studies of H. MEERWEIN, *Ann.* **455**, 227 (1927); *Ber.* **66**, 441 (1933), as well as L. J. KLINKENBERG and J. A. KETALAAR, *Rec. trav. chim.* **54**, 959 (1935).

[8] According to the systematic investigations of R. Scholder, the amphoteric behavior of metal hydroxides is due entirely to the formation of hydroxo compounds. For instance, sodium stannite should be formulated $[Sn(OH)_3]Na$, and similar formulas are valid for aluminates, zincates, *etc.*

exhibit the equivalence of the inorganically and organically bound oxygen atom with respect to its coordination capacity on the same metal atom.

Certain complex compounds contain several metal atoms (in some cases also non-metallic atoms) that function as coordination centers and are linked to each other by common attached groups. Such compounds are known as *polynuclear complexes*. Polynuclear chromium compounds are produced by heating chromium hydroxide with acetic acid; green, water-soluble, basic chromic acetates with the composition

$$Cr_2(C_2H_3O_2)_7(OH)_2 \text{ (I)} \quad \text{and} \quad Cr_3(C_2H_3O_2)_8(OH) \text{ (II)}$$

result. These acetates have the remarkable property that in (I) *one* acetate radical, and in (II) *two* acetate radicals can be replaced by equivalent quantities of other acid radicals so that in the resulting compounds there are always six acetate radicals to each three chromium atoms. Consequently, these radicals must be linked with the three chromium atoms to form a stable complex. This is also indicated by the fact that the precipitation of the chromium hydroxide is delayed for some time if ammonia is added to aqueous solutions of the basic acetates, either warm or at room temperature. The coordination formula of the polynuclear cation contained in the basic chromic acetates accordingly is:
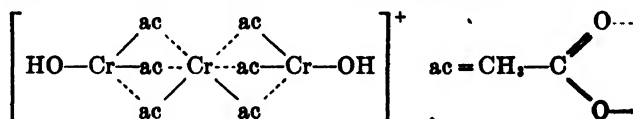
This is an example of an auxiliary valence ring of the third kind (see p. 25). This cation is also formed by warming complex chromium salts with excess sodium acetate, and this procedure causes the chloride or sulfate radicals (see p. 71), that previously were bound non-ionogenically to the chromium, to be liberated. They thus regain their normal precipitability by silver nitrate and barium chloride, respectively.

Ether and ketones, especially, form complexes readily. This action is not surprising since they are organic derivatives of water. The compounds of ketones with stannic chloride, which is particularly prone to form complexes, are, for the most part, of very simple composition, approximating the formula
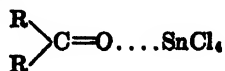
The probable reason for this simplicity is that there is not space enough to permit the grouping of several large organic molecules around a metal atom. Similarly, even among the numerous purely organic complex

compounds, there never occur such high coordination numbers as are the rule with molecular compounds; the molecular ratio is usually 1:1, 1:2, or 1:3. However, even in organic complex compounds certain atoms or groups of atoms must surely be regarded as coordination centers.

Acido Compounds

The isomeric hydrates of chromic chloride (see p. 31) were shown to contain non-ionogenic chlorine atoms. There are analogous hydrates of chromic sulfate with sulfate radicals bound non-ionogenically. Their formation is the reason for the incomplete precipitation of sulfate by barium chloride in the presence of chromium salts. Numerous complex compounds have acid radicals in the first sphere grouped around a metal atom. These are known as *acido groups* or *acido compounds*, respectively.

Particular interest attaches to acido compounds containing only acid radicals of the same kind coordinated in the first sphere. Such compounds often form under conditions that are met in actual analyses, and then permit their analytical utilization.

An acido compound that is very stable, even in the solid state, is cryolite, $AlF_3 \cdot 3NaF$, whose coordination formula, $Na_3[AlF_6]$, exhibits the attachment of the six fluorine ions to the aluminum atom. An analogous complex ferric fluoride is also known. The anion $[Fe F_6]^{---}$ forms so rapidly in aqueous solution and dissociates so slightly into ferric and fluoride ions that an acid ferric solution, after the addition of sodium fluoride, gives no red coloration with thiocyanates.

The cyanide ion shows a particularly great tendency to form stable acido compounds. The solubility of numerous metal hydroxides and cyanides in excess potassium cyanide is due to the formation of compounds with complex metal cyanide anions. Examples are: $K_2[Cu(CN)_3]$; $K[Ag(CN)_2]$; $K_4[Fe(CN)_6]$; $K_3[Fe(CN)_6]$.

The best known of these are the complex cyanides of iron, namely, the yellow and red prussiates, $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$. The corresponding hydroferrocyanic and hydroferricyanic acids are very strong in contrast to hydrocyanic acid, which is volatile and only slightly soluble in water. These two acids are quite stable even in the solid state. The complex anion $[Ag(CN)_2]^-$, which can be formed even at extremely low concentrations of silver ion, dissociates so slightly into its components that not only silver chloride, bromide, cyanide, and thiocyanate, but even the still less soluble silver iodide is soluble in potassium cyanide. Among the water-soluble complex cyanides, special mention will be made of the derivatives of quadrivalent molybdenum and tungsten. The central atom has the unusual coordination number of 8 in the compounds $K_4[Mo(CN)_8]$ and $K_4[W(CN)_8]$.

The thiocyanate ion can also form acido compounds. The complex $[Hg(CNS)_4]^{--}$ ion, that is present in a solution containing mercuric ions plus a thiocyanate, forms crystalline heavy metal salts, some of which are highly colored.

The blue color produced by cobalt salts and potassium thiocyanate in the presence of alcohols and ketones, is due to the formation of potassium cobaltothiocyanate, $K_2[Co(CNS)_4]$. It is used analytically to detect cobalt and thiocyanate. The red complex $[Fe(CNS)_6]^{---}$ ion, which is the basis of the well known test for ferric or thiocyanate ions, is of this same type.

The compounds $K_2[HgI_4]$ and $K[BiI_4]$, formed by dissolving the corresponding heavy metal iodides in excess potassium iodide, are used analytically. The alkaline solution of the former is the familiar Nessler's reagent for ammonia.[9] The bismuth compound is intensely yellow and permits a colorimetric determination of this element. The formation of acido compounds with halogen hydracids is the basis of the solubility of silver chloride in concentrated hydrochloric acid and in concentrated solutions of alkali chlorides, as well as of the solubility of silver iodide and other silver halides in a concentrated solution of potassium iodide. Such solutions, from which silver chloride or iodide precipitate on dilution with water, contain the compounds $H[AgCl_2]$, $Na[AgCl_2]$, $K[AgI_2]$, respectively, or their ions. Well crystallized $Cs_2[AgCl_3]$ can be isolated from the solution of silver chloride in cesium chloride. Examples of acido compounds of soluble metal halides are stable $H_2[CeCl_6]$ and $H[FeCl_4]$. It is the formation of this latter ether-soluble compound that makes it possible to extract ferric chloride from water solutions containing HCl.

Acido compounds of several oxygen acids are also known. The solubility of barium sulfate in concentrated sulfuric acid or fused sodium sulfate is due to the formation of $H_2[Ba(SO_4)_2]$ and $Na_2[Ba(SO_4)_2]$, respectively. The production of the complex ferriphosphoric acid, $H_3[Fe(PO_4)_2]$, is shown by the fact that ferric solutions, whose color is yellow because of hydrolysis, immediately become colorless on the addition of phosphoric acid, and by the discharge of the color of red ferric thiocyanate by phosphoric acid. The acido compounds include the double oxalates. Only the aluminum salt, $Na_3[Al(C_2O_4)_3]$, is specifically mentioned here, because its formation can be used analytically.[10]

[9] M. L. NICHOLS and C. O. WILLITS [*J. Am. Chem. Soc.* **56**, 769 (1934)] showed that the yellow-brown compound precipitated from Nessler's solution by ammonia has the empirical formula $Hg_2I_3NH_2$. Accordingly, the previous assumption that it is Hg_2ONH_2I (oxydimercuriamido iodide) is incorrect. The oxygen-free compound can be regarded either as the addition compound $HgI_2 \cdot HgNH_2I$, or as mercuritriiodoamido mercuriate, $Hg[HgNH_2I_3]$.

[10] Compare F. FEIGL, Spot Tests, p. 473.

Hydrogen sulfide can also form acido compounds. Production of such alkali salts is the reason for the solubility in alkali sulfides of the "acid sulfides" of arsenic, antimony, tin, mercury, molybdenum, and tungsten. Typical examples are $Na_2[HgS_2]$ and $Na_2[SnS_4]$.

Sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$, shows that the nitrite ion can function as a complex ligand in acido compounds. The aqueous solution of this salt is a well known reagent for potassium. This compound again exemplifies the fact that anomalous valency and unstable forms of linkage can be stabilized by complex formation (see pp. 30, 50).

COORDINATION OF ELEMENTS

The compounds (see page 29) of the alkaline earth metals with ammonia contain the metals in the elementary state as the carriers of the attached neutral portions. Since, in addition, it is probable that certain intermetallic compounds ($NiCd_4$, $NaHg_4$, *etc.*), and the metal carbonyls ($Ni(CO)_4$, $Fe(CO)_5$, $W(CO)_6$, *etc.*), the metal nitro compounds (*e.g.*, $2\ Cu \cdot NO_2$),[11] and the iron nitrosyls[12] $Fe(NO)_4$ and $Fe(NO) \cdot 2CH_3OH$, are to be viewed as coordination compounds, it follows that free atoms or molecules can also form complex compounds. The formation of complex compounds of free metals is of no significance in analytical chemistry; on the other hand, the coordination of nonmetals is important.

The *polyhalides* and *polysulfides*, in which elementary halogens or sulfur occur as attached coordinated groups, have considerable analytical significance as reagents.

Iodine dissolves in pure water to only a very slight degree (approximately 0.027 g. in 100 g. H_2O at 15°C.). It dissolves very easily in aqueous solutions of alkali iodides and produces brown to yellow solutions. On the other hand, the solubility of potassium iodide in organic solvents is raised considerably by iodine. Hence, the formation of a compound of elementary iodine and alkali iodide is indicated. The triiodides MeI_3 (Me = K, Rb, Cs, NH_4) are known even as solids. They can be considered as addition compounds of iodine and the respective metal iodide. AgI_3 and HgI_6 are examples of insoluble triiodides. Attention is directed to the fact that numerous organic bases, the alkaloids for instance, are likewise precipitated as triiodides by the addition of potassium iodide solution of iodine to the aqueous solution of their salts. These triiodides contain the least iodine of the polyiodides. Pentaiodides (*e.g.*, CsI_5), heptaiodides (*e.g.*, KI_7), and enneaiodides (*e.g.*, CsI_9) are known. In any case, a mixture of various polyiodides must be assumed

[11] P. SABATIER and J. SENDERENS, *Ann. chim. phys.* [7] **7**, 348 (1896).
[12] W. MANCHOT and E. ENK, *Ann.* **470**, 275 (1929); W. MANCHOT and H. GALL, *ibid.* **470**, 271 (1929).

to be present in the aqueous solution of iodine plus potassium iodide. The coordinated iodine retains its reactivity in the polyiodides. The solution of iodine in potassium iodide makes it possible to prepare more stable standard solutions of iodine for use in volumetric analysis. The coordinated iodine in water-insoluble polyiodides (*e.g.*, of polyatomic organic bases) also reacts with sodium thiosulfate, and the respective hydroiodides remain. The general coordination formula of polyiodides is $Me[I(...I_2)_x]$, in which x = 1 to 4. The iodine molecules are linked to the iodine ion by auxiliary valences. For example,

$$CsI_5 = Cs\begin{bmatrix} & & I_2 \\ I & & \\ & & I_2 \end{bmatrix}$$
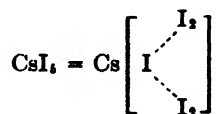
There are also polyiodides in which elements other than the iodide ion function as carriers of the elementary iodine. Thus iodine is much more soluble in solutions of mercuric chloride than in water, probably because of coordination on the slightly dissociated $HgCl_2$.

The excellent solubility of iodine in hydrobromic acid indicates the existence of the acid, $HBr...I_x$. In the compound $CsBrI_2$, as well as in the diazonium compound $C_6H_5N_2ClI_2$, it is doubtless the bromine or chlorine atoms that accomplish the linking of the iodine. In the iodine compound of trimethylamine and of quinoline, the halogen is probably coordinated on the nitrogen atom:
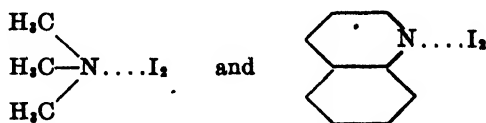
The sulfur atom carries the iodine in diethyl sulfide periodide, $(C_2H_5)_2S \cdot I_2$. Probably an oxygen atom is the coordinator of the iodine in the dark brown dextrin compound, $(C_6H_{10}O_5)_6I_2$. The same, in all likelihood, is true in the familiar blue starch-iodine complex, whose solution exhibits practically no iodine tension at room temperature.[13]

Polybromides are also known, but in considerably fewer numbers than polyiodides. Polychlorides do not seem to exist.

The similarity between iodine and sulfur, which also shows itself in numerous organic compounds, is emphasized by the fact that the polysulfides, in which a sulfur atom or a sulfur ion carries the elementary

[13] Starch-iodine solutions are quite stable even after heating. This is shown by the fact that the blue color disappears on boiling, but returns with almost the original intensity when cooled. Compare K. ZEPF and F. VETTER, *Mikrochemie*, Emich Festschrift, 1930, p. 280.

sulfur, are close parallels of the polyiodides. Alkali polysulfides are produced by dissolving sulfur in alkali sulfides. The analogy to the polyhalides is shown also by the general coordination formula,

$$Me_2[S(\ldots S_x)], \text{ where } x = 1 \text{ to } 8$$

The series Na_2S_2 (sulfur-yellow), Na_2S_4 (orange-red) and Na_2S_5 (dark yellow) shows that the color of polysulfides deepens with increasing sulfur content. The analogy between the polyiodides and the polysulfides is further shown by the fact that both classes of compounds in the solid or dissolved state will give up much of their coordinated element to a suitable solvent, carbon disulfide for instance.

The addition of dilute acids causes the alkali polysulfides to decompose with formation of hydrogen sulfide and precipitation of sulfur. The acids from which they are derived are not stable, but, under certain conditions, liquid H_2S_2 and H_2S_3 can be isolated. The acidity of the parent acid, hydrogen sulfide, is increased considerably by the coordination of sulfur. This is shown by the fact that the hydrolysis of all of the sodium polysulfides is less than that of sodium monosulfide. In 0.1 N solution, the hydrolysis at 25°C. of the various sodium sulfides is:

$$Na_2S \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 86.4\%$$
$$Na_2S_2 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 64.6\%$$
$$Na_2S_3 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 37.6\%$$
$$Na_2S_4 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 11.6\%$$
$$Na_2S_5 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 5.7\%$$

Elementary sulfur can also be coordinated on other atoms. In $CHI_3 \cdot 24S$ and $AsI_3 \cdot 24S$, obviously eight sulfur atoms are linked to each iodine atom of the iodoform and the arsenic triiodide, respectively.

The solution of free selenium and tellurium in concentrated sulfuric acid is due to the coordination of these elements:

$$Se + H_2SO_4 \rightarrow Se \cdot SO_3 + H_2O$$
$$Te + H_2SO_4 \rightarrow Te \cdot SO_3 + H_2O$$
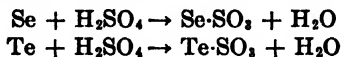
A green or red solution, respectively, results because of the formation of loose addition compounds between selenium or tellurium and the anhydride of sulfuric acid. These compounds are decomposed into their components by water, and red selenium or black tellurium precipitates. Hence, the compounds are only stable in excess concentrated sulfuric acid, which serves as a dehydrating agent. Selenium and tellurium can be detected with the aid of these coordination compounds.
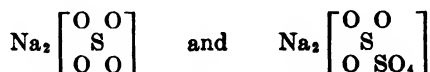
The hydrates $Cl_2 \cdot 8H_2O$ and $Br_2 \cdot 10H_2O$ can be regarded as instances of the coordination of elements. These products can be isolated in the solid state. The excellent solubility of chlorine and bromine in water is probably due to the formation of these hydrates.
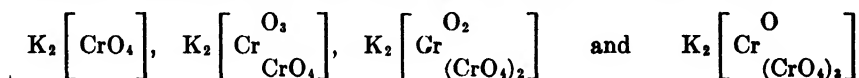
POLYACIDS

When sodium bisulfate is fused it loses water easily and forms sodium pyrosulfate:

$$2NaHSO_4 \rightarrow H_2O + Na_2S_2O_7$$
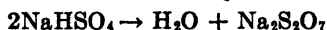
The product can be considered as either an addition product of Na_2SO_4 and SO_3, or a derivative of sodium sulfate in which one oxygen atom is replaced by the sulfate group. The formal relation between sodium sulfate and sodium pyrosulfate is shown by the coordination formulas:

$$Na_2 \begin{bmatrix} O & O \\ & S \\ O & O \end{bmatrix} \quad \text{and} \quad Na_2 \begin{bmatrix} O & O \\ & S \\ O & SO_4 \end{bmatrix}$$

The polychromates exhibit an analogous relation to each other:

$$K_2 \begin{bmatrix} CrO_4 \end{bmatrix}, \quad K_2 \begin{bmatrix} O_3 \\ Cr \\ CrO_4 \end{bmatrix}, \quad K_2 \begin{bmatrix} O_2 \\ Cr \\ (CrO_4)_2 \end{bmatrix} \quad \text{and} \quad K_2 \begin{bmatrix} O \\ Cr \\ (CrO_4)_3 \end{bmatrix}$$

In borax, $Na_2B_4O_7$, a similar association of an acid anhydride with the alkali salt of the same acid can be assumed if sodium tetraborate is written as an addition compound of sodium metaborate and boric anhydride: $2NaBO_2 \cdot B_2O_3$.

These salts are derived from *polyacids*. Those in which oxygen atoms are replaced by the acid radical of the *same* acid are called *isopolyacids* in distinction of the *heteropolyacids* in which a different acid radical or anhydride has been coordinated.

The polyacids of molybdenum and tungsten are of particular interest. For instance, if a neutral or alkaline solution of Na_2MoO_4 is acidified, there result at certain pH values, in abrupt stages, more highly aggregated anions, such as $Mo_3O_{11}^{----}$, $Mo_6O_{21}^{------}$. This has been proven by measurements of the conductivity and studies of other physical constants.[14]

Heteropolyacids are formed especially easily by the oxides of molybdenum, tungsten and vanadium, with phosphoric, arsenic, and silicic acids.[15]

Phosphates react with ammonium molybdate in acid solution to product a yellow precipitate:

$$(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 6H_2O \rightleftharpoons (NH_4)_3H_4[P \cdot (Mo_2O_7)_6]4H_2O$$
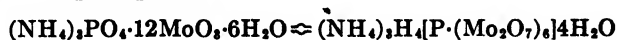
This compound may be regarded as the ammonium salt of the water-soluble heteropolyacid, $H_7[P(M_2O_7)_6]$. It is derived from a hypothetical

[14] G. JANDER, K. JAHN and W. HENKESHOVEN, Z. anorg. allgem. Chem. **194**, 383 (1930).

[15] Compare the comprehensive discussion of polyacids by A. ROSENHEIM in R. ABEGG, Handbuch der anorganischen Chemie **4**, 977 (1920).

phosphoric acid $H_7[PO_6] = H_3PO_4 \cdot 2H_2O$ by replacement of all the oxygen by the divalent Mo_2O_7 group. Compounds are also known in which only several of the oxygen atoms of this hypothetical phosphoric acid are replaced by Mo_2O_7 groups.

Analogous compounds are derived from arsenic and silicic acid, and from germanium dioxide.[16] The corresponding free heteropolyacids can be formulated $H_7[As(Mo_2O_7)_6]$, $H_8[Si(Mo_2O_7)_6]$, and $H_8[Ge(Mo_2O_7)_6]$. The previous formulation of the heteropolyacids has been rejected by Jander[17] on the basis of diffusion experiments. He assumes that the Mo_2O_7 group is not present in the complex, but rather that the complex anion $[H_2PO_4 \cdot (H_3Mo_6O_{21})_2 \cdot xH_2O]^{------}$ is formed.

The heteropolyacids just discussed consist of acids of quinquevalent elements and acid anhydrides of sexivalent elements. There are also heteropolyacids derived from divalent and sexivalent elements. Furthermore, acids of the same oxidation levels also combine with each other; for instance, sulfuric acid with selenic, chromic, and molybdic acid.

In the heteropolyacids of phosphorus, silicon, germanium, and arsenic, the coordinated Mo_2O_7 groups exhibit enhanced reactivity toward numerous reducing agents (see p. 115). This characteristic forms the basis for sensitive tests for phosphates, silicates, and germanium.

An insoluble compound that probably has the character of a heteropolyacid is $H_2[TiO_2SeO_3]$. It is produced by precipitating Ti^{IV} with SeO_2, and loses no water when heated to 100°.[18]

Heteropolyacids whose anions consist of two acid anhydrides from the 6th group of the periodic system are known.[19] Examples are $H_2[CrO_3 \cdot SO_4]$, $H_2[CrO_3 \cdot SeO_4]$ or their K-, Na-, NH_4-, Ba-, Sr-, and Ca-salts. The light brown precipitate that appears, after long standing, in the familiar sulfuric acid-dichromate mixture, used for cleaning glassware, is due to the sodium or potassium salts of the foregoing acid. It is formed by the reaction of sulfuric acid with potassium dichromate to produce K_2SO_4, which then takes up CrO_3.

Heteropolyacids in which inorganic acid anhydrides are combined with organic acids are quite noteworthy, and have some analytical importance. Typical instances are salicylmolybdic acid, $H_2[C_6H_4(O)(COO) \cdot MoO_3]$ and the two oxalomolybdic acids, $H_2[C_2O_4 \cdot MoO_3]$ and $H_2[C_2O_4 \cdot 2MoO_3]$. The MoO_3 molecules are probably coordinated on the oxygen of the carboxyl group. The interferences with the reactions of molybdic acid by oxalic and tartaric acid (p. 75), and conversely of the organic acids

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[16] R. SCHWARZ and H. GIESE, *Ber.* **63**, 2428 (1930).

[17] G. JANDER and H. WITZMANN, *Z. anorg. allgem. Chem.* **215**, 310 (1933).

[18] R. BERG and M. TEITELBAUM, *Z. anorg. allgem. Chem.* **189**, 101 (1930).

[19] J. MEYER and V. STATECZNY, *Z. anorg. allgem. Chem.* **122**, 1 (1922).

by molybdic acid, doubtless are due to the formation of heteropolyacids of this type. The quantitative precipitation of molybdic acid[20] and likewise of considerable quantities of tungstic and vanadic acid by benzoinoxime in acid solution can probably be ascribed to the formation of insoluble heteropolyacids. The same applies to the precipitation of tantalum and niobium pentoxides by this reagent. This behavior of benzoinoxime, $C_6H_5C(OH)C(NOH)C_6H_5$, indicates that in organic compounds acidic-NOH groups as well as carboxyl groups can function in the formation of heteropolyacids.

INNER COMPLEX COMPOUNDS

All of the types of complex compounds that have been discussed in the foregoing sections include instances in which organic neutral portions have a coordination capacity due to the activity of certain atoms. In view of the variety of organic compounds, it is natural to inquire into the behavior of such compounds as contain not only coordinating atoms, but also salt-forming groups. Aminoacetic acid, $CH_2(NH_2)COOH$, also known as glycine, is an instance. Its copper salt, that can be formed by the action of copper acetate, behaves in several respects as a complex compound. Copper glycinate, (I) in contrast to copper acetate, is no longer capable of adding ammonia; its aqueous solution has only a low electrical conductivity; it shows the deepening of the color toward blue that is observed in the aqueous solution of all copper ammine salts. These properties indicate that copper glycinate is far more comparable to the ammoniate of copper acetate (II) than to the parent compound. The following coordination formulas illustrate this relation:
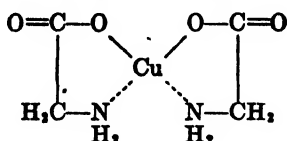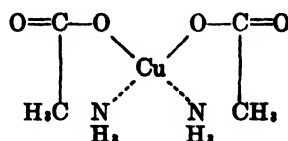

(I)   (II)

Salts in which a metal atom manifests auxiliary valences toward certain atoms of the acid radical are called *inner complex salts*. This term was proposed by Ley.[21] Pfeiffer (p. 26) calls them auxiliary valence rings of the first kind. An argument supporting this formulation of the inner complex copper glycinate is given by the copper salt of aminodiacetic acid.[22] This compound (III)

[20] H. KNOWLES, *Bur. Standards J. Research* **9**, 1 (1932).
[21] H. LEY, *Z. Elektrochem.* **10**, 954 (1940).
[22] J. DUBSKY and M. SPRITZMANN, *J. prakt. Chem.* **96**, 113 (1917).

NH₂

O—Cu—O

O=C   C=O

C—N—C

H₂ H H₂

(III)
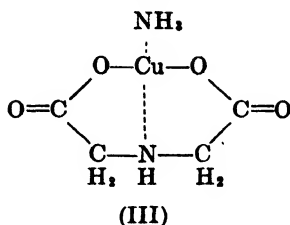
is the bridge from the diammine of copper acetate (II) to copper glycinate (I). Only one ammonia molecule is coordinated in it, and the inner molar linkage of the nitrogen atom of the imide group replaces the coordination of a second ammonia molecule.

The coordination formula of copper glycinate shows that inner complex salts contain ring systems. The Baeyer strain theory holds for their stability exactly as it does for purely organic cyclic compounds. Consequently, the possibility of producing such cyclic salts depends on the relative position of the salt- and the complex-forming groups. Stable compounds are only to be expected when an atom can form part of a five- or six-membered ring.
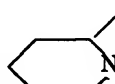
Metal compounds in whose molecules a metal atom, through binding, has become a member of a ring, are known as chelate compounds.[22a] The binding may occur through two principal valences, through two auxiliary valences, or through one principal and one auxiliary valence. Hence, inner complex salts are a definite type of chelate compounds.

Because of their particular linkage relationships, most inner complex salts are non-electrolytes. The saturation of the combining power of the metal atom by several atoms of the same molecule obviously can inhibit both a dissociation and an addition of water molecules and, consequently, a hydration (which, in turn, is related to the solubility in water). The introduction of metal atoms into inner complex salts often brings out the organic character of these compounds, which then manifests itself by the persistence of the insolubility in water, solubility in organic liquids, and by the fact that such products often can be sublimed or distilled without decomposition. It need not be emphasized that the solubility characteristics of compounds are of great significance to the analyst. But no less important is the additional circumstance that inner complex salts are frequently colored, or that a deepening in color may accompany their formation from colored components.

The production of inner complex ring systems depends not only on the salt- and complex-forming groups being in a position suitable for ring closure, but largely also on the nature of the metal atoms that are linked as they are in salts. Thus the copper salt of aminoacetic acid is a typical

[22a] G. T. MORGAN and H. D. DREWS, *J. Chem. Soc.* **117**, 1456 (1920).

inner complex compound, while its zinc and cadmium salts, on the basis of their conductivity in aqueous solution, cannot be so considered, even though a coordination of ammonia molecules on zinc and cadmium salts exists in numerous other compounds.   On the other hand, as shown by

the behavior of α-picolinic acid, , and other analogous compounds, a nitrogen atom linked cyclically in the α-position to a carboxyl group is no longer capable of forming inner complex salts with copper. However, such compounds always produce soluble, colored inner complex salts with ferrous salts.   Accordingly, many distinctive properties of metals not observed in the normal salts appear upon the formation of inner complex salts.   This consideration is of great weight with respect to the specific or selective action of organic reagents.

Inner complex salts of organic compounds with acidic characteristics, in which a coordination can occur on nitrogen or oxygen atoms, are encountered most frequently.   The copper salts of other α- and β-amino carboxylic acids correspond to copper glycinate with respect to the coordination on nitrogen.

It appears that the nitrogen atoms of oxime ($=NOH$) groups are particularly endowed with auxiliary valences.   The α-dioximes of the general formula:

$$R\text{---}C\text{=}NOH$$
$$R\text{---}C\text{=}NOH$$
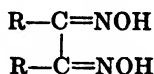
form the analytically valuable, insoluble colored inner complex salts with nickel and palladium.   According to Pfeiffer,[23] the insoluble red nickel salt of diacetyldioxime (dimethylgloxime) has the structure:
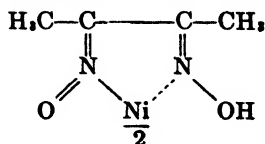

The metal is directly bound to the nitrogen atoms of both oxime groups, to one by a principal valence, to the other by an auxiliary valence, so that a five-membered ring results.

A similar ring is present in the salts of 2-pyridylphenyl-[24] and 2-pyridylmethyl ketoxime.[25]   This is shown by their coordination formulas:

[23] P. Pfeiffer, *Ber.* **63**, 1813 (1930); *cf.* also *ibid.* **61**, 103 (1928), and *J. prakt. Chem.* [2] **124**, 137 (1930).

[24] L. Tschugaeff, *Ber.* **39**, 3382 (1906).

[25] B. Emmert and K. Diehl, *Ber.* **62**, 1738 (1929).

and
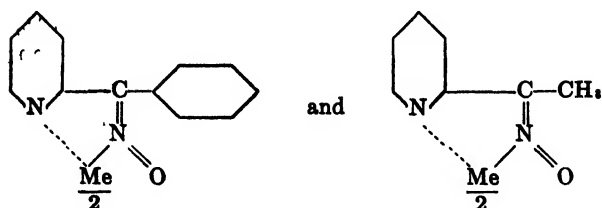
Inner complex salts are formed by rubeanic acid, (I) $H_2N \cdot CS \cdot CS \cdot NH_2$, in its diamide- or acid-form (II).[26] The insoluble colored copper, cobalt, and nickel salts of this compound afford sensitive tests for these metals.[27] They have the coordination formula (III):

$$H_2N-C-C-NH_2 \qquad HN=C-C=NH \qquad HN=C\underline{\qquad}C=NH$$

(I) (II) (III)   (Me = Cu, Co, Ni)
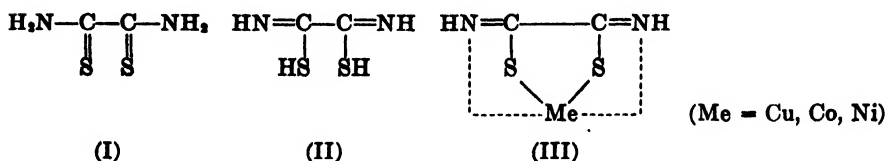
Symmetrical dimethyl- and diphenylrubeanic acids behave like the parent compound.[28]

The urea derivates diphenylcarbohydrazide(I) and diphenylcarbazone (II) form typical inner complex salts,[29] that correspond to (III):

(I) (II) (III)
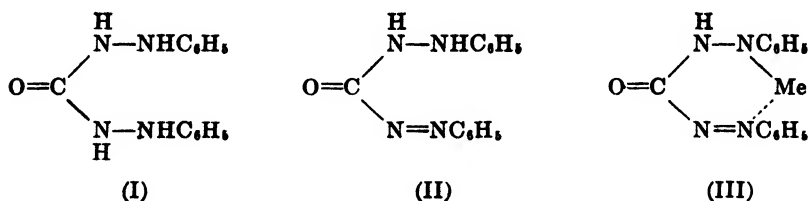
The same is true of diphenylthiocarbazone (dithizone). Numerous studies by Fischer[30] have shown that many heavy metal salts of this reagent (IV) have characteristic colors and are easily soluble in organic liquids. These properties are advantageous for the analytical employment of these salts. The inner complex salts of dithizone can be given the following coordination formulas, corresponding to the keto form (V) and enol form (VI) of this extremely useful reagent:
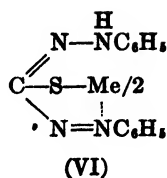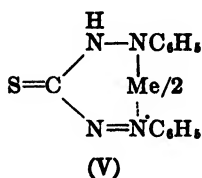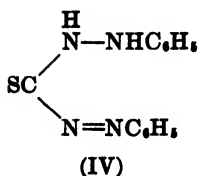
[26] P. RÁY and H. BAHR, *J. Indian Chem. Soc.* **5**, 497 (1928).
[27] F. FEIGL, Spot Tests, p. 118.
[28] F. FEIGL and R. BADIAN, unpublished studies.
[29] F. FEIGL and F. LEDERER, *Monatsh.* **45**, 63, 115 (1924).
[30] Compare the compilation by H. FISCHER, *Z. angew. Chem.* **46**, 442 (1933).

$$
\begin{array}{ccc}
\overset{H}{N}\!-\!NHC_6H_5 & \overset{H}{N}\!-\!NC_6H_5 & \overset{H}{N}\!-\!NC_6H_5 \\
SC & S\!=\!C\quad Me/2 & C\!-\!S\!-\!Me/2 \\
N\!=\!NC_6H_5 & N\!=\!NC_6H_5 & N\!=\!NC_6H_5 \\
(IV) & (V) & (VI)
\end{array}
$$

The behavior of 8-hydroxyquinoline ("oxine") shows that cyclic bound nitrogen atoms in a phenol can participate in the formation of inner complex salts. This compound (I), forms difficultly soluble salts with numerous metals. These products were shown by Hahn, and especially by Berg, to afford numerous new methods of determination and separation.[31] The constitution of the inner complex salts of 8-hydroxyquinoline with bivalent metals is represented by (II)


(I)   (II)
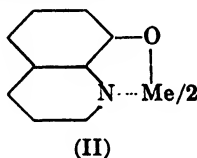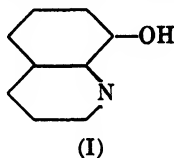
The slightly soluble, inner complex salts of quinaldic acid (III) with bivalent metals (copper, cadmium, zinc, iron) are similarly constituted.[32] The metal atom forms a five-membered ring with the nitrogen atom and the carboxyl group, as shown in (IV)

(III)   (IV)
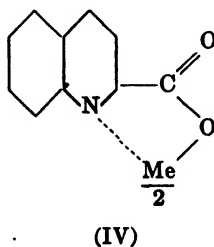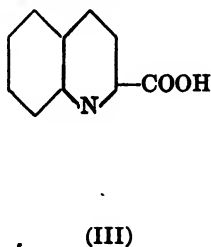
The heavy metal salts of quinaldic acid can be used for quantitative determinations and separations.

The acido compounds containing oxalate radicals (see p. 75) can be regarded as compounds with an *inner complex anion*. As shown by the coordination formula of sodium aluminum oxalate:

$$
\left[Al\left(\begin{array}{c} O\!=\!C\!-\!O \\ | \\ O\!-\!C\!=\!O \end{array} \right)_3 \right] Na_3
$$
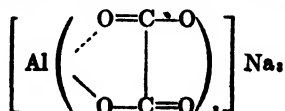
[31] Compare F. HAHN and K. VIEWEG, *Z. anal. Chem.* **71**, 122 (1927); *Z. angew. Chem.* **39**, 1198 (1926); also R. BERG, Das *o*-Oxychinolin "Oxin." Sammlung: *Die chemische Analyse*, p. 34. Stuttgart, 1935.

[32] P. RÁY and M. BOSE, *Z. anal. Chem.* **95**, 400 (1933).

the auxiliary valency is localized on one oxygen atom of the carboxyl group.

Numerous inner complex salts of α- and β-hydroxy acids are known. The following formulas show that they contain stable rings of five or six members:


and
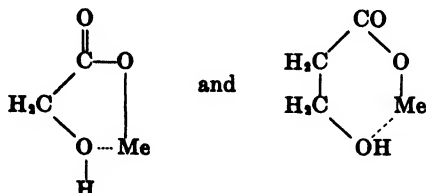
Compounds of this type are present in Fehling's solution and in Nylander's solution. These tartrated solutions of copper and bismuth hydroxide, respectively, in potassium hydroxide are well known reagents. When warmed with reducing sugars, they precipitate cuprous oxide or metallic bismuth.

Aromatic hydroxy acids are particularly prone to form inner complexes. The violet color observed when ferric salts are mixed with salicylic acid (I) is due to the formation of the complex represented by (II):


(I)   (II)
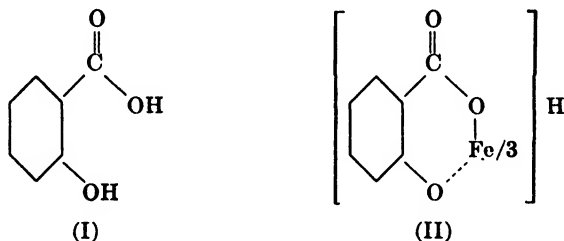
This compound, as well as the sodium aluminum oxalate (see p. 45), indicate that the formation of inner complex ring systems is not confined to non-electrolytes, but that soluble compounds with inner complex anions can also be formed. Di- and polyhydroxy compounds also form inner complex compounds: the hydrogen of one hydroxyl group is replaced by metal and this is then coordinated on the oxygen of a second hydroxyl group. The pyrocatechol compound of ferric iron is an example:
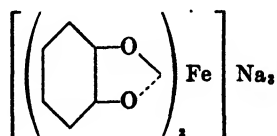

1,3-diketones, $R \cdot CO \cdot CH_2 \cdot CO \cdot R$, in their enol form, $R \cdot C(OH){:}CH \cdot CO \cdot R$,

combine with numerous metals to form inner complex salts of the general formula:


Me = 1 equivalent of metal
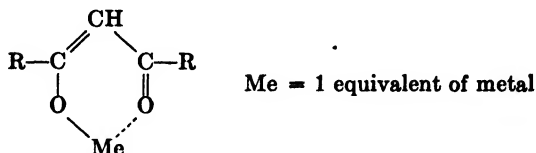
Some of these salts are distinguished by remarkable stability. For instance, the aluminum salt of acetylacetone can even be volatilized without decomposition.

An atomic grouping similar to that in the enol forms of the 1, 3-diketones is present in those hydroxyanthraquinones that have an hydroxyl group in the α-position. Alizarin,
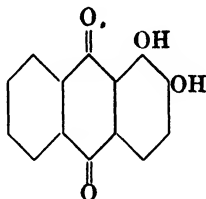
for instance, can form inner complex compounds with metal salts as well as with acids. An example of the former is the compound with $SnCl_4$ (I), prepared by Pfeiffer,[33] and of the latter, the boroacetic ester (II), isolated by Dimroth and Faust:[34]

(I)   (II)
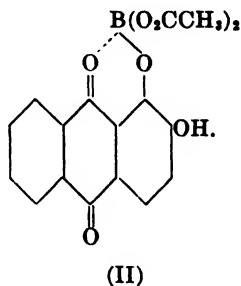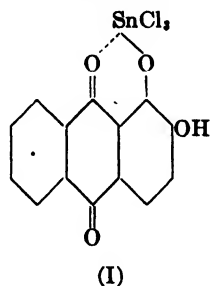
The coordination of a boron atom on the oxygen atom of a CO group in hydroxyanthraquinones is probably the reason why an intense color change occurs when borates are added to the sulfuric acid solution of various hydroxyanthraquinones. This effect can be used for the detection of boron.[35] The presence of groups that tend to form inner com-

[33] P. Pfeiffer, Ann. 398, 137 (1913).
[34] O. Dimroth and T. Faust, Ber. 54, 3020 (1921).
[35] F. Feigl, Spot Tests, p. 257.

plexes is doubtless of decisive importance for the formation of the color lakes of hydroxyanthraquinones, which probably are, in part, adsorption compounds of the metal hydroxides and the dyes.

It may be assumed that 1-hydroxyanthraquinone (and also alizarin) is itself an inner complex hydrogen compound
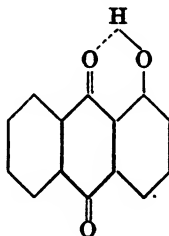
This viewpoint is supported by the anomalous behavior of the hydroxyl group in the ortho position. It is much more difficult to esterify than the hydroxyl groups in other positions, and normally does not form salts. This is shown by the insolubility of 1-hydroxyanthraquinone in alkalies. Sidgwick (see p. 397) has shown that inner complex hydrogen compounds are present in all organic hydroxylated compounds (alcohols, phenols, enols) that have CO, NO_2, or $N=N$ groups in the ortho position. In such compounds it is possible for the H atom to be coordinated on the O or N atoms. This coordination is revealed by the solubility relationships, which are abnormal in comparison with those exhibited by the isomeric or tautomeric compounds.

The behavior of α-nitroso-β-naphthol (I) has considerable interest as an inner complex salt former. It forms inner complexes in its tautomeric, orthoquinoidal form (II). The inner complex cobalt, copper, iron, *etc.*, salts are shown as coordination compounds in (III):
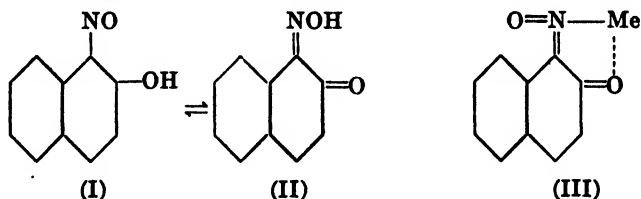
The water-insoluble inner complex salts of α-nitroso-β-naphthol, without exception, are colored. (The same is true of the analogous isomeric salts of β-nitroso-α-naphthol.) Some of these salts, particularly the zirconium and cobalt compounds, have analytical significance. It should be noted that α-nitroso-β-naphthol reacts with cobalt salts to form a mixture of cobaltous and cobaltic nitroso-naphtholate. The oxidation

of the divalent to trivalent cobalt is at the expense of the nitroso compound. The higher valence of the cobalt is conserved in the inner complex salt.

Nitrosophenylhydroxylamine (I), known as "cupferron," was one of the first organic reagents through which the great value of forming inner complex salts for purposes of quantitative analysis was demonstrated. Its analogue, α-nitrosonaphthylhydroxylamine (II), is called "neocupferron." These names are due to the fact that their water-soluble ammonium salts precipitate the corresponding copper and ferric salts quantitatively from acid solutions. These voluminous flocculent precipitates are inner complex salts (III):
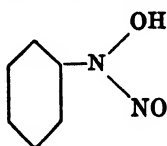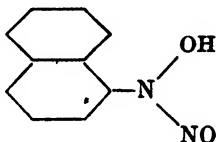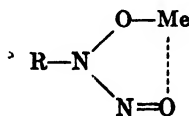
(I)　　　　　　　(II)　　　　　　　(III)

Other metals can also be precipitated from acid solutions by these reagents.[36]

The fact that normally unstable compounds can be stabilized through complex formation is again demonstrated among the inner complex salts. Thus Pfeiffer and his collaborators[37] showed that o-hydroxyaldehydes, (e.g., salicylaldehyde) and o-hydroxyketones (e.g., o-hydroxyacetophenone) can be converted easily into inner complex salts of o-hydroxyaldimines (I) and o-hydroxyketimines (II):
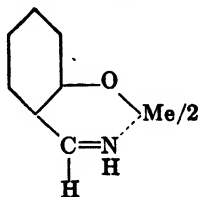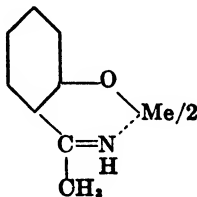
(I)　　　　　　　　　　(II)

This stability is achieved even under conditions—in aqueous ammoniacal solution (with Cu, Ni and Zn salts)—at which the imines are ordinarily

[36] O. BAUDISCH, Chem. Ztg. **33**, 1928 (1909); O. BAUDISCH and S. HOLMES, Z. anal. Chem. **119**, 16 (1940). The analytical applications of cupferron and neucupferron are discussed by W. PRODINGER, Organic Reagents in Quantitative Inorganic Analysis, translated by S. HOLMES, Nordeman Publishing Company, New York, 1940. See also G. F. SMITH, Cupferron and Neocupferron, G. F. Smith Chemical Company, Columbus, 1938.

[37] P. PFEIFFER, E. BUCHHOLZ and O. BAUER, J. prakt. Chem. **126**, 163 (1931).

not stable (see p. 347). The cobaltic salt of α-nitroso-β-naphthol, (see p. 48) shows that abnormal valences of metals can be stabilized in inner complex salts. Other interesting examples of this have been discovered by Barbieri[38] in the divalent silver salt of α-picolinic acid (I) and by Burada[39] in the divalent silver salt of quinolinic acid (II);

(I)   (II)
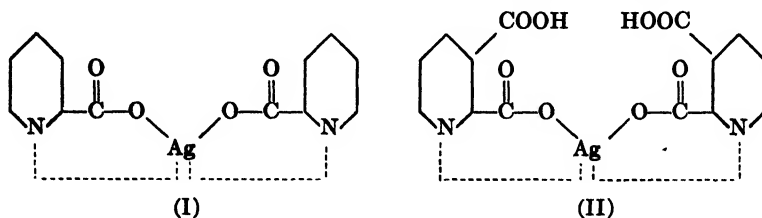
The formation of all the inner complex compounds hitherto discussed requires that the acid hydrogen atoms which can be replaced by metal atoms be in such spatial proximity to coordinating atoms or atomic groups of the same molecule that an activation of auxiliary valences or binding forces can occur. Acidic organic compounds especially afford the possibility of such inner molecular principal or auxiliary valence activation with ring closure. Because of the lack of a suitable number of prospective ring members, the ring closures characteristic of inner complex salts are possible only in exceptional cases among purely inorganic compounds.[40] Consequently, addition or intercalation compounds predominate among these. Inner complex compounds are especially important with regard to their analytical employment, because the formation of principal and auxiliary valence rings is frequently accompanied by anomalous solubility or tinctorial qualities, or by both. These consequences often are very important for the sensitivity of a reaction which leads to the production of compounds with these properties. Furthermore, the auxiliary valences active in inner complex compounds may bring out effects that can be of significance to the specificity or selectivity of a reaction.

[38] G. BARBIERI, *Chem. Abstracts* **28**, 2291 (1934).

[39] A. BURADA, *Chem. Abstracts* **30**, 2129 (1936).

[40] O. RUFF and E. KRÖHNERT [*Z. anorg. allgem. Chem.* **114**, 203 (1920)] have isolated the compound (I) which, on the basis of its behavior, can be regarded as an inner complex salt with the structure (II)   .

(I)   (II)

The great variety of organic compounds and the possibility of introducing acidic groups, as well as groups endowed with auxiliary valences, into the molecules of organic compounds make it certain that the possibilities have not been exhausted with the compounds now known. Other inner complex compounds of analytical value will doubtless be discovered. In any event, the considerations of coordination chemistry have led to definite conceptions regarding the relations between the grouping of atoms and specific combining effects and have opened a new field of analytical research (compare Chapters VI–IX).

ORGANIC MOLECULAR COMPOUNDS

With the exception of the inner complex compounds just discussed, in which a particular class of metal salts of organic acids dominates, all other types of complex compounds should be amenable to separation, in accordance with their modes of formation, composition, and coordination formulas, into components that are capable of independent existence and reactivity. This separation is occasionally actually realizable by heating, but far oftener it is brought about by chemical action. In the latter case, the components exhibit their normal reactivity but, in certain instances, this is impaired or masked to varying extents (compare Chapter IV). Since the smallest units, both of complex compounds and their independent components, are invariably molecules, in principle it would seem logical and it should be permissible to speak of them as combinations of molecules, i.e., as molecular compounds. However, this is not the case in actual practice because in the terminology of complex chemistry this designation is reserved for a special class of compounds. The distinguishing characteristic of the members of this class is that they contain molecules of organic compounds combined with molecules of other organic compounds or with molecules of inorganic compounds, and usually in the molecular ratio 1:1 or 1:2. Such combinations, which can be separated into their components quite easily, are called organic molecular compounds. However, it is more correct to distinguish between the organic-organic and the organic-inorganic molecular compounds.

In the strict sense, only those combinations which conform to the Avogadro molecular concept should be accepted as molecular compounds. In other words, the term should be restricted to molecular compounds in the gaseous state, or in the quasi-gaseous state (dilute solutions of solutes in indifferent solvents). Such true molecular compounds have been frequently found in solutions, melts, and vapors. However, in ordinary usage the term molecular compounds likewise includes solid products, in which there has been consummated an association of true molecular

compounds in a crystal lattice. Consequently, in this case, as in the other types of complex compounds that have been discussed in the preceding sections, particular emphasis is laid on the combination of the components in definite, stoichiometric ratios. This is justified as a guiding principle in the classification of these materials as it serves to differentiate the various types.[41]

Many organic molecular compounds show a marked similarity to complex compounds that have already been considered. For example, molecular compounds between metal salts and alcohols, or between metal salts and organic amines, are direct homologues of hydrates and ammoniates. They often are quite similar with respect to stability and the ways in which they can be prepared. However, the great majority of organic molecular compounds exhibit two characteristics which place them in a separate category. In the first place, they usually are less stable toward chemically active solvents and frequently even toward seemingly indifferent organic liquids. Secondly, they are ordinarily prepared in organic media. This latter fact is not surprising because, in general, water is not a suitable solvent for the organic components of inorganic-organic molecular compounds, or for the two organic components in purely organic molecular compounds. However, still another factor seems to play a role along with the difference in the nature of the formation medium. Aqueous solutions contain chiefly the ionically dispersed form of the solute, whereas the molecular dispersed form predominates in organic media. Consequently, it seems logical to assume that the molecules are the active reactants in organic solutions. Thus the designation "molecular compound" acquires a real meaning also with respect to the conditions surrounding the preparation of these compounds.

It has been estimated that several thousand organic molecular compounds are known. This number includes only those that can be given a definite stoichiometric composition on the basis of the analysis of isolable · products, or by deduction from physical measurements made on their solutions. The formation of organic molecular compounds plays an important part in solution processes (see Chapter VIII). In addition, these compounds often serve as intermediates or pre-combinations ante-

[41] This classification takes no account of the relations between the linkage state of the components in a complex compound and its form of aggregation. The existence of such relations is evident from the following considerations. The individual molecules of complex compounds of the general and simplest formula AB are held together solely by the forces operating between A and B, whereas, in the crystal lattice, forces between A and A and B and B are important in holding the lattice together. A detailed discussion of this question, which is intimately connected with the linkage mechanism in crystalline and dissolved complex compounds, is beyond the scope of this book. See F. EPHRAIM, *op. cit.* (p. 28) and G. BRIEGLEB, *op. cit.* (p. 28).

cedent to the occurrence of deeper-seated reactions of the components. Finally, organic molecular compounds can enter as entities into chemical reactions with other materials. Apart from their production in solution processes, organic molecular compounds are of significance in analytical chemistry if their formation can be discerned through characteristic alterations in solubility or by the appearance of characteristic color effects. The latter result is often called halochromism. Such color reactions play a role especially in organic analysis, and this also seems to be the chief field of application of reactions that lead to the formation of organic molecular compounds. It should be noted that combinations of medicaments frequently are organic molecular compounds and as such may be the subject of analytical investigations.

As was the case in all the complex compounds treated in the earlier sections, the coordinative linking in organic molecular compounds can be located on certain atoms of the particular reaction partners. The following are especially important as coordination centers in molecules of organic compounds:[42]

(a) H atoms in OH groups of alcohols, phenols, and carboxylic acids;

(b) O atoms in OH groups of alcohols, phenols, and carboxylic acids; in ketones and ethers; in CO groups of COOH groups;

(c) S atoms in SH groups of mercapto compounds and thiocarboxylic acids; in the thioketones and thioethers; in disulfides;

(d) N atoms in primary, secondary, and tertiary amines; in acid amides, nitriles, nitro and nitroso compounds; in azo and diazo compounds;

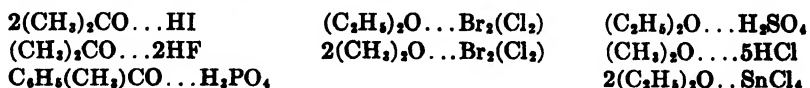(e) C atoms in ethylenic and aromatic compounds.

Strictly speaking, coordination among organic molecular compounds thus always requires the presence of certain groups containing coordinatable atoms. If an organic compound possesses two such active groups, it consequently has two potential coordination centers. In addition, when an organic compound possesses an active group (OH, NO_2, *etc.*) which includes two coordinatable atoms, it may combine with one and the same compound to produce distinctly different molecular compounds. The latter are isomers of each other, and their constitution is determined by which of the active atoms is involved in the coordinated linkage.[43] As

[42] The coordination ability of Se, Te, P, and halogen atoms in organic compounds is disregarded here. The number of known molecular compounds of this kind is relatively quite few.

[43] Even such simply constructed compounds as HCl and H_2O reveal the fact that molecules of compounds can possess two different coordination centers. In $AuCl_3 \cdot HCl$ written as $[AuCl_4]H$, the Cl atom is doubtless bound coordinatively. On the other hand, in $NH_3 \cdot HCl$, formulated as $[NH_3H]Cl$, the H atom of HCl is coordinatively bound. A comparison of $[Me(OH_2)_2]Cl_2$ and $[NH_3H]OH$ shows that, in the H_2O molecule, the O atom as well as one H atom, can function as a coordination ligand.

will be seen presently, it is possible among aromatic compounds to have coordination on unsaturated or doubly bound carbon atoms, or coordinative linkage may be due to the sum total of the unsaturated carbon atoms. Consequently, consideration must be given not only to the functioning of active groups contained in aromatic compounds, but also to the action stemming from unsaturated carbon atoms.   These are the reasons why the coordination center cannot always be located with certainty in organic molecular compounds containing aromatic components.   Influences which have not yet been clearly elucidated determine whether or not organic compounds with active groups will undergo coordinative binding and, if so, where this linkage will occur.   Among these determinants are: the influence on the active atomic group exerted by the rest of the molecule of an organic compound; the influence of solvents and other reaction conditions; the influence of a second reactant, which itself is capable of coordination.   The net result of this interplay of influences is that various molecular compounds can often be formed side by side. Although much empirical knowledge is available concerning organic molecular compounds, there are, as yet, no rules for the sure prediction as to when, and in what systems, the formation and isolation of organic molecular compounds can be expected.   The sole guiding principle is that the molecule of the organic compound must contain at least one active group.   Careful consideration of the experience gained in analogous cases is also an aid.   Certain typical examples of organic molecular compounds will be given to illustrate the foregoing general remarks.

Coordination on oxygen atoms of organic compounds is exhibited in the following molecular compounds:

$2(CH_3)_2CO\ldots HI$	$(C_2H_5)_2O\ldots Br_2(Cl_2)$	$(C_2H_5)_2O\ldots H_2SO_4$
$(CH_3)_2CO\ldots 2HF$	$2(CH_3)_2O\ldots Br_2(Cl_2)$	$(CH_3)_2O\ldots.5HCl$
$C_6H_5(CH_3)CO\ldots H_3PO_4$		$2(C_2H_5)_2O\ldots SnCl_4$

Among the etherates, the bromine (chlorine) compounds merit special attention because the production of such addition compounds is related to the excellent solubility of free halogens in ether.   The monoetherate of sulfuric acid is entirely analogous to its monohydrate.   This is shown by the fact that the heat effect (*circa* 6.8 cal.) is practically the same when the addition compound is formed with one mol of water or ether.

The compound between benzoic anhydride and sulfuric acid

$$(C_6H_5CO)_2O\ldots H_2SO_4$$

is comparable to the etherate of sulfuric acid.   However, benzoic anhydride and sulfuric acid also combine in the ratios 1:2 and 2:1.   The fact that two components can form addition compounds in more than one

molecular ratio is a common occurrence among organic molecular compounds. As already noted, this is also the case with other classes of complex compounds, such as hydrates, ammines, heteropoly acids, *etc.*
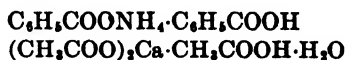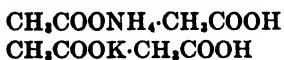
A coordinate binding between oxygen and hydrogen atoms is assumed in the foregoing molecular compounds of acids. The same holds for molecular compounds between phenols and acids. Representative examples are:

$$2C_6H_5OH\ldots H_2SO_4 \qquad C_6H_5OH\ldots H_2C_2O_4$$
$$C_6H_5OH\ldots CCl_3COOH \qquad C_{10}H_7OH\ldots H_2C_2O_4$$
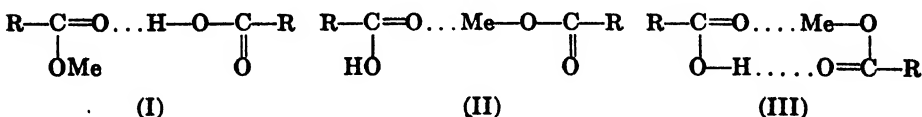$$C_6H_4BrOH\ldots H_3PO_4 \qquad 2C_{10}H_7OH\ldots H_2C_2O_4$$
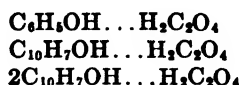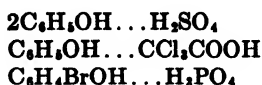
In these instances there has been a combination of molecules of acidic compounds. This shows that the production of organic molecular compounds is not a matter of effecting a union by virtue of the basic and acidic nature of the components. This fact becomes even more distinctly evident in the "double acids," such as $C_6H_5COOH\ldots H_2SO_4$ (m.p. 87°) and $C_6H_5COOH\ldots CHCl_2COOH$. In these, the oxygen atom of the CO group probably furnishes the coordination ligand, *e.g.*,

$$C_6H_5C\!\!\begin{array}{c} OH \\ \diagdown \\ O\ldots HX \end{array}$$
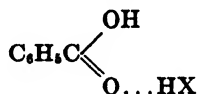
Such double acids are closely allied to the acid salts of monocarboxylic acids. Examples are:

$$CH_3COONH_4\cdot CH_3COOH \qquad C_6H_5COONH_4\cdot C_6H_5COOH$$
$$CH_3COOK\cdot CH_3COOH \qquad (CH_3COO)_2Ca\cdot CH_3COOH\cdot H_2O$$

The coordination formulas of such acid salts must take into account an auxiliary valence linkage between oxygen atoms and acidic hydrogen atoms, and also an auxiliary valence binding between oxygen and metal atoms. Thus, the possibility of isomers arises as shown in (I), (II), and (III):

$$\begin{array}{ccc} R\!-\!C\!=\!O\ldots H\!-\!O\!-\!C\!-\!R & R\!-\!C\!=\!O\ldots Me\!-\!O\!-\!C\!-\!R & R\!-\!C\!=\!O\ldots.Me\!-\!O \\ | \qquad\qquad\qquad \| & | \qquad\qquad\qquad \| & | \qquad\qquad\quad | \\ OMe \qquad\qquad\quad O & HO \qquad\qquad\quad O & O\!-\!H\ldots.O\!=\!C\!-\!R \\ (I) & (II) & (III) \end{array}$$

Analogous coordination formulas may be valid for other organic molecular compounds of carboxylic acids. If the acidic hydrogen atoms of acid salts are replaced by metal atoms, the result is the production of purely organic double salts containing the same acid radical in both components. An instance is the double salt $(CH_3COO)_2Pb\cdot CH_3COONa$. If hydrogen atoms are put in place of the metal atoms, coordination

formulas for double molecules of acids are obtained. A coordinative linkage between oxygen and hydrogen analogous to that shown in (I) and (III) may be assumed also in the molecular compounds of phenols with each other, and likewise between tertiary alcohols and various phenols, naphthols, nitrophenols, *etc.* Examples are:

$$C_6H_5OH \cdot 2C_6H_4(OH)_2 \text{ (}m\text{- and }p\text{-)}; \quad (CH_3)_3COH \cdot 2C_6H_5OH$$
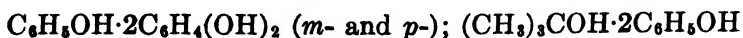
The combination between phenols forms the bridge to associated forms of phenols and brings up the probability that, in essence, association forces are identical with auxiliary valence forces. The coordinative ability of the CO group is still more marked in aldehydes and ketones than in carboxylic acids. Numerous aldehydes, and some ketones, form molecular compounds with alcohols, phenols, and acids. The general formulas of these products are $R \cdot CHO \ldots HO\text{-}R$ and $R \cdot CHO \ldots HOOC\text{-}R$. In them there is obviously coordination of acidic hydrogen atoms on the oxygen atoms of the CO group. Additional evidence is the fact that acetone can bind two molecules of phenol, but has no combining capacity for phenolic ethers. The ability of the phenolic hydrogen atom to coordinate with a ketone group is shown also in the behavior of phenols toward aromatic aminoketones. Thus Michler's ketone,

$$(CH_3)_2NC_6H_4\text{-}CO\text{-}C_6H_4N(CH_3)_2$$

adds phenols but not phenolic ethers. Consequently, it dissolves in phenols with a deepening of color which can be used to reveal the presence of free phenols in phenol ethers. Likewise, acid amides, such as urea, add phenols but not phenol ethers.

The following inorganic-organic molecular compounds exemplify coordination on sulfur atoms. Thioethers, of the general formula R_2S, combine with Cu_2Cl_2, $AuCl$, and $AgNO_3$ in the molecular ratios 1:1 and 1:2. Among divalent metals, addition compounds are known in which $Ni(CNS)_2$, CdI_2, and HgI_2 combine with thioethers in the ratios 2:1 and 1:1. Thioketones, R_2CS, form compounds with Cu_2Cl_2, $HgCl_2$, and BiI_3 in the ratios 2:1 and 1:1. Thiourea is quite prone to coordinate. By means of its sulfur atom it can occupy one coordination position of metal atoms in metal halides. Since ammonium halides and the chlorides of thallium, cesium, and potassium usually display little tendency to form complexes, it is rather remarkable that they do add four molecules of thiourea. Even mercuric chloride, which dissociates but slightly when dissolved in water, can take on four molecules of thiourea. The chlorine atoms of the product are completely ionizable. This substantiates the formula $[HgThi_4]Cl_2$, (Thi = thiourea). $HgCl_2 \cdot 2Thi$ is also known; this water-soluble addition compound is a non-electrolyte.

Coordination on nitrogen atoms is assumed in all addition products of primary, secondary, and tertiary amines with acids. These compounds of organic bases are analogous to ammonium salts. Furthermore, a number of instances have been found in·which free iodine adds directly to organic nitrogen bases. The meriquinoid compounds of benzidine and its homologues (see p. 333) are of analytical interest. In these there is a union of one molecule of a *para* quinoidal oxidation product of benzidine with one molecule of an amine:

$$H_2N\!\!-\!\!\langle\rangle\!\!-\!\!\langle\rangle\!\!-\!\!NH_2\cdot HN\!\!=\!\!\langle\rangle\!\!=\!\!\langle\rangle\!\!=\!\!NH$$
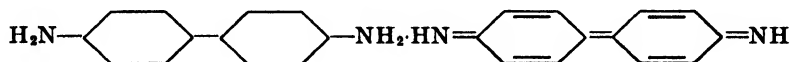
These molecular compounds between amine and imine, which, in addition, contain acid, are deep blue.

The nitrogen atoms in azo compounds are also capable of coordination. For instance, cuprous chloride forms red molecular compounds with aliphatic azo compounds, $R\!-\!N\!\!=\!\!N\!-\!R$, in the ratios $1:1$ and $2:1$.

Molecular compounds containing aromatic nitro derivatives (mono- and polynitro compounds) are quite numerous (about 800). The combinations with aromatic hydrocarbons and their hydroxy and amino derivatives are usually in the molecular ratio $1:1$. The following tabulation demonstrates that the introduction of OH, NH_2, *etc.*, into benzene leads to a deepening of the color of the corresponding molecular compound. This type of group effect on intensifying color is known as auxochromism.

$R(NO_2)_x\ldots C_6H_6$	colorless
$R(NO_2)_x\ \ldots C_6H_5OH$	yellowish
$R(NO_2)_x\ldots C_6H_5NH_2$	orange
$R(NO_2)_x\ldots C_6H_5NHCOCH_3$	yellowish
$R(NO_2)_x\ldots C_6H_5N(CH_3)_2$	blood-red

The first of this series is often regarded as the parent compound. The assumption is that there is a coordination of one NO_2 group, or its nitrogen atom, on a carbon atom of the benzene molecule, or on one of its carbon double bonds.
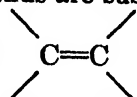
Picric acid enters into purely organic molecular compounds by coordination on the OH group or through coordination on one of the NO_2 groups. Accordingly, there are two series of picric acid addition compounds with primary amines; they differ in color:

$(NO_2)_3C_6H_2OH\ldots NH_2R$ yellow
$HOC_6H_2(NO_2)_3\ldots NH_2R$ dark colored
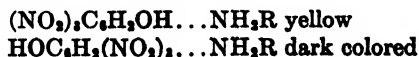
Aliphatic nitro compounds are strikingly less capable of coordination than aromatic nitro compounds. Tetranitromethane, $C(NO_2)_4$, is a notable exception. Its solutions in paraffine hydrocarbons are colorless,

but it dissolves with color production in unsaturated hydrocarbons and likewise in liquids having an enolic structure. Doubtless the formation of molecular compounds of tetranitromethane is responsible for this solution color, which can be used as the basis of a test for carbon double bonds in organic compounds.

Coordinative binding effected through carbon atoms should be taken into account when considering molecular compounds whose components contain none of the active groups cited on p. 53. Such components include hydrocarbons and halogenated hydrocarbons especially. The compound $(C_6H_5)_3COH\ldots CCl_4$, and other addition compounds of carbon tetrachloride, demonstrate that coordination ·among organic molecular compounds can occur directly on a carbon atom.[44] It is probable, but as yet unproved, that coordination takes place directly on a definite carbon atom in organic molecular compounds in which one component is a hydrocarbon. It has been found almost invariably that only those hydrocarbons containing carbon double bonds are susceptible

of coordination. In the simplest case, ethylene, the $\diagdown C{=}C \diagup$ linkage

should accordingly provide two equivalent carbon atoms as binding centers. Benzene contains three such linkages and theoretically its six carbon atoms should thus be capable of coordination, if, for the time being, the binding is localized on a single carbon atom. However, it developed that each ethylene molecule in complex compounds occupies only one coordination position. This is shown by a comparison of $PtCl_2\cdot 2NH_3$ and $PtCl_2\cdot NH_3\cdot C_2H_4$. Obviously, one molecule of C_2H_4 (with two doubly bound carbons) has taken the place of only one NH_3 molecule. An analogous replacement of one NH_3 molecule by one molecule of an aromatic hydrocarbon is found in $Ni(CN)_2\cdot NH_3\cdot C_6H_6$. (Toluene, furan, or aniline can be substituted here for benzene.) The benzene compound is derived from $[Ni(NH_3)_4][Ni(CN)_4]$ by the replacement of two NH_3 molecules by two C_6H_6 molecules. The light yellow crystalline product is formed by shaking an ammoniacal solution of nickel cyanide, i.e., a solution containing the preceding compound, with benzene or an alcoholic solution of benzene.[45] This finding is in good agreement with the binary formulation $[Ni(NH_3)_2(C_6H_6)_2][Ni(CN)_4]$. The platinum and nickel compounds just cited are not true molecular com-

[44] The stable molecular compound between carbon tetrachloride and rotenone is used for the isolation and quantitative determination of this important insecticide. The components are present in the ratio 1:1. Compare H. A. Jones, *Ind. Eng. Chem., Anal. Ed.* 9, 206 (1937).
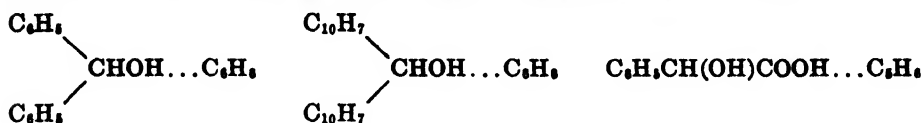
[45] The process is used to determine benzene in crude benzol. Compare K. A. Hofmann and collaborators, *Ber.* 39, 1149 (1906).

pounds; they are intercalation or addition compounds. They are used here to illustrate the rather rare coordinative binding of hydrocarbons on metal atoms, and especially to exemplify the fact that a molecule of a hydrocarbon can occupy only one coordination position, regardless of its number of double bonds.

$$2SbCl_3\ldots C_6H_6;\quad SbCl_3\ldots C_6H_5CH_3;\quad 2SbI_3\ldots C_6H_5\cdot C_2H_5$$

are regarded as true molecular compounds. A selective coordinative binding capacity of the antimony atom toward aromatic hydrocarbons is exhibited here. In the preceding examples of coordination of unsaturated hydrocarbons, the question is still unanswered as to whether a carbon

atom of a $\diagdown C\!=\!C \diagup$ group occupies one coordination position, or whether

the total affinity field of the carbon double bond is active. This question remains open also with respect to other molecular compounds of hydrocarbons. The following purely organic instances can be cited:

$$\begin{array}{c}C_6H_5\diagdown\\[2pt]\qquad CHOH\ldots C_6H_6\\[2pt]C_6H_5\diagup\end{array}\qquad\begin{array}{c}C_{10}H_7\diagdown\\[2pt]\qquad CHOH\ldots C_6H_6\\[2pt]C_{10}H_7\diagup\end{array}\qquad C_6H_5CH(OH)COOH\ldots C_6H_6$$

The hydrogen atom of an alcoholic or phenolic OH group is probably bound to benzene in these compounds. In contrast, the tertiary hydrogen atom is, in all likelihood, the coordination ligand for R in the compounds $(C_2H_5)_3CH\ldots R$ (R = benzene, aniline, furfurol, carbazole).

The carbon atom of carbon monoxide probably has a coordinative binding capacity for metal atoms. This is evidenced in $K_3[Fe(CN)_5CO]$ and also in $PtX_2\cdot CO$, $PtX_2\cdot 2CO$, and $RuX_2\cdot 2CO$ (X = Cl, Br, I, S). This capacity also appears in $Cu_2Cl_2\cdot 2CO\cdot 4H_2O$ and $Cu_2SO_4\cdot 2CO$. These molecular compounds play a part in gas analysis, because their formation is responsible for the absorption of carbon monoxide by acidified or ammoniacal cuprous solutions.

The composition of molecular compounds leaves no doubt that coordinative bindings are possible through the agency of carbon atoms. This view is strengthened by the fact that many ethylenic and aromatic hydrocarbons give characteristic color reactions with salts and acids (especially concentrated sulfuric and phosphoric), whereas saturated hydrocarbons (both open chain and cyclic) give completely negative responses. These colored products have not been isolated and hence their composition has not been established. There is no doubt, however, that organic molecular compounds are involved, since the organic components are usually regenerated unaltered if these colored liquids are diluted with water.

COMPLEX COMPOUNDS OF UNDEFINED STOICHIOMETRIC COMPOSITION

The most characteristic representatives of the various types of complex compounds, as discussed previously, are encountered as isolable products which are often crystalline. Nevertheless, the isolation of stoichiometrically defined combinations of materials that of themselves are stable cannot be taken as the sole characteristic property of complex compounds. It must be remembered that the possibility of precipitating compounds of every kind, *i.e.*, those produced through the activity of principal valences as well as complex compounds, is by no means dependent merely upon the heat effect attending their formation in-homogeneous solution. The possibility of the deposition of a solid always involves, in addition, the energy of the lattice, *i.e.*, the type of binding holding the components in the crystal lattice, the velocity at which nuclei are formed, and the atomic and molecular volumes of the components. Accordingly, it is readily understandable why there are complex compounds whose existence can be detected only in solution or in melts, and furthermore, why the stoichiometric composition of complex compounds may differ according to their particular state of aggregation or dispersion. This signifies that a material which has a stable stoichiometric composition in the crystalline or amorphous state may be unstable in solution, and, conversely, a form that is stable in solution may not be capable of existing as a solid. In addition, molecular compounds which have a certain composition in solution may be transformed, when they are dissolved or melted, into another composition characteristic of the dissolved or molten state.[46] Finally, many instances are known in which two molecular species under given conditions simultaneously produce several complex compounds of different compositions. Accordingly, a constant stoichiometric composition is by no means the sole characteristic of complex compounds produced from two molecular species which can exist separately. A far more general characteristic of complex compounds is the demonstrable activity of intermolecular forces. Such activity is revealed by the fact that combinations which are regarded as complex compounds exhibit quite definite and reproducible deviations from the properties of their parent components. These divergences can be detected either by chemical or physical (optical or electrical) methods, or by both. Consequently, combinations produced by intermolecular forces (auxiliary valences) should also be included among complex or

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[46] For instance, F. FEIGL and R. KOBLIANSKY [*Ber.* **58**, 1483 (1925)] found that methyl oxalate and phenol, by the usual method, form the addition compound $(CH_3)_2C_2O_4 \cdot C_6H_5OH$, whereas R. KREMANN and coworkers [*Monatsh.* **45**, 368 (1924)] showed that $(CH_3)_2C_2O_4 \cdot 4C_6H_5OH$ is the sole product in melts.

coordination compounds, even though they have not been isolated, and, hence, a formula showing the definite molecular proportions of their components cannot be given.

There are two main groups of stoichiometrically undefined complex compounds. The first includes combinations whose existence can be established in solution only. The second group comprises water-insoluble combinations, formed mostly by the wet method. Compounds dissolved in water that are closely related to the isolable hydrates are in the first group. The solid hydrates of metal salts, which are usually crystalline, as a rule are not identical with the hydrates present in dilute solutions. The aqueous solutions of dissociable salts contain hydrated ions, whose water content is much greater than that of the corresponding solid salt. Furthermore, many anhydrous metal salts exist as hydrated ions after they are dissolved. The influence of the state of aggregation and the degree of dispersion on the retention (coordination) of water molecules is thus plainly exhibited. The addition of water, when compounds dissolve in this liquid, and the crystallization of hydrated compounds from aqueous solutions, is paralleled by the union of molecules of alcohol, ether, and other organic solvents to compounds that are dissolved in these organic liquids. Such union of molecules of the solvent with those of a solute is known as solvation. The evaporation of organic solutions, or crystallization or precipitation from organic solvents, often produce stoichiometrically defined compounds of the solute and solvent, or precipitates containing molecules of the solvent are obtained. The molecules of alcohol, ether, benzene, *etc.*, that are built into a crystal lattice often behave, with respect to their retention there, analogously to water molecules that make up part of such structures, since the addenda can usually be eliminated by raising the temperature. As water-soluble hydrates are merely considered to be members of a sub-group of the much larger class of solvates, it is clear that both stoichiometrically definable and undefinable hydrates exist, and also that this differentiation holds for all solvates. The formation of solvates is quite important when materials dissolve in "indifferent" solvents, which, from the viewpoint of coordination chemistry, are not indifferent at all since, when solvates are formed, molecules of solvent always add to molecules of a solute. Constitutional factors, and particularly the presence of coordinable atoms in the molecules of solute and solvent, play a considerable role in these additions (see Chapters VIII and IX).

Sometimes the formation of a solvate is directly apparent because of the production of characteristic solution colors. Color reactions often occur when hydrocarbons, amines, and other organic compounds dissolve in concentrated sulfuric acid. Frequently, such colors are discharged on

adding water or other diluents, and the compound that dissolved with production of the color is then recovered unchanged. In such cases, the existence of colored solvates can be assumed with certainty, even though their composition has not been defined, because they have not been isolated in a form suitable for analysis. Such undefined solvates are also present in solutions of iodine in indifferent organic solvents. These solutions are always either violet or brown. The brown solutions doubtless involve a coordination of iodine molecules on certain atoms of the solvent. This statement is supported by the observation that the addition of solid organic compounds, that are soluble in the solvent, or of organic liquids that are miscible with the solvent, often causes the violet solution to change toward brown, provided the added material possesses atoms (oxygen, nitrogen, sulfur) that can coordinate iodine. The solvates of iodine in ether can be given the coordination formula $(C_2H_5)_2O$ ... $(I_2)x$, which implies that no definite statement can be made concerning the value of x. Analogous formulas can be written for solutions of iodine in other solvents possessing oxygen atoms. It is noteworthy that iodine in brown solutions is more reactive in certain chemical changes than the same quantity of iodine in violet solutions (see p. 121). This clearly indicates that iodine complexly bound in these brown solvates is more reactive than iodine in violet solutions, where the iodine molecules probably are more loosely bound to the molecules of the solvent, or where the iodine molecules possibly are in a condition that corresponds to that of iodine vapor, which likewise is violet. It is quite possible that, whenever a solvent exerts a definite influence on the chemical reactions occurring in it, as in the case involving iodine just cited, the effect is due to solvate formation, *i.e.*, to coordination of one of the reactants with molecules of the solvent. This signifies that chemical changes do not proceed simply and unswervingly in the milieu of a solvent, but rather that the latter takes an active part in the reaction.

The most important methods for the formation and isolation of complex compounds are based on the actions of materials in true solution, where they are molecularly or ionically dispersed. Nevertheless, the activity of intermolecular forces is not limited to these states of dispersion. Associated molecules in solution, as well as polymerates of molecules whose size approximates colloidal particles, are also subject to the action of auxiliary valence forces. It has been established that colloidal solutions are never completely free of electrolytes, and that the retention of ions and the related development of the electrical double layer is primarily responsible for the stability or, more correctly, the semi-stability of colloidal dispersions of metals and their compounds. Wo.

Pauli[47] and his school, through their careful experimental studies, are principally responsible for the projection of coordination chemical concepts into the realm of colloids. For instance, according to Pauli, colloidal particles of silicic acid should be regarded as addition compounds of SiO_2 particles on ionized silicic acid. The purified dialyzed silicic acid sol, prepared from sodium silicate and hydrochloric acid, is given the formula $[x(SiO_2 \cdot aq) \cdot ySiO_3H^-] + yH^+$, in which the relation x:y can be assumed to have values from 600 to 1500.[48] Fundamentally analogous formulae are given by Pauli to other colloidally dispersed particles. An important value of his formulation is that it expresses the complex chemical character of colloidally dissolved particles, and pictures the linkages between molecular polymerates and carrier ions.

If molecular aggregates whose size is of the order of colloidal particles are presumed to be built up by the union of like molecules until they reach the size of visible crystalline or amorphous phases, it does not follow that this process is necessarily accompanied by a loss of the ability to bind like or unlike molecules or ions. The solid crystalline or amorphous state is itself an expression of the cohesion of molecules through intermolecular forces. Every molecule in the interior of a solid is surrounded on all sides by like molecules, that are arranged in orderly fashion in crystals, and in a disorderly manner in amorphous materials. Such molecules, which are hedged in on all sides, are fully saturated with respect to their binding power. In contrast, the molecules at the free surface are unsaturated in this respect, and consequently can exert binding forces directed outward. According to Haber[49] and Langmuir,[50] adsorption, i.e., the retention of gaseous or dissolved materials by solids, should be viewed as due to the action of auxiliary valences exerted by the surface molecules of the solid phase. In adsorption on crystal surfaces as well as on amorphous solids (powders, foils, wires), there is always a tremendous disproportion between the quantity of the adsorbent and that of the adsorbate. This is quite understandable, since binding occurs only on molecules of the free surface. This disproportion would disappear, and also simple relations with respect to the molar quantities would be attained, as in isolable molecular compounds, if consideration were limited to the molecular species that actually are directly bound to each other in adsorption. This, however, is not practical, i.e., it is

[47] Wo. PAULI and E. VALKO, Elecktrochemie der Kolloide, Vienna, 1929.
[48] Wo. PAULI and E. VALKO, Kolloid-Z. **36**, 325 (1925); **38**, 289 (1926).
[49] F. HABER, Z. Elektrochem. **20**, 521 (1914).
[50] I. LANGMUIR, J. Am. Chem. Soc. **38**, 2221 (1916); **39**, 1848 (1917); **40**, 1361 (1918).

impossible without precise measurements of the free surface.[51] It is therefore expedient to treat the experimentally measurable total result of an adsorption as a complex compound that cannot be stoichiometrically defined.

The adsorption of solutes on the surface of crystalline or amorphous precipitates that are formed in the solution is highly important in analytical procedures. Many anomalies in precipitation operations and occasional difficulties in obtaining pure precipitates are related to adsorption processes. This will be discussed in Chapters V, X, and XI. It will suffice here merely to point out that an adsorption is not determined solely by the availability of a free surface, Adsorption often exhibits a specific or selective character since it depends, among other factors, on the chemical nature of the particular adsorbent and the material that is being adsorbed. It should also be remembered that the adsorption of minute quantities of material sometimes is accompanied by characteristic color changes. This point may have significance in certain analytical procedures.

Special attention should be given to adsorption on gelatinous materials, whose web-like structure presents a large internal surface. Another important phenomenon is the mutual adsorption of colloidally dispersed particles carrying opposed electrical charges. This leads to flocculation. The results of such unions of materials, in which there is not so great a disproportion between the components as exists when materials are adsorbed on surfaces that are not so highly developed, are often known as adsorption compounds. In these cases also, there is no constant numerical relationship between the molecules of the components. The composition of these adsorption complexes, for the most part, is quite dependent on the conditions under which they are produced. There are many stages between adsorption and adsorption compounds on the one hand, and, on the other, between adsorption compounds and stoichiometrically defined compounds produced by the action of principal or auxiliary valence forces. There is no uniformity in the chemical literature, with respect to differentiating combinations produced by adsorption. From the standpoint of coordination theories, all combinations that result from adsorption, *i.e.*, from auxiliary valence binding to surface molecules, can be viewed as complex compounds that are not stoichiometrically defined.

[51] Calculations of the thickness of adsorption films have been made on suitable systems. They were based on measurements of the free surface and determinations of the quantity of material adsorbed. In the majority of cases, the film is monomolecular, which is in accord with Langmuir's theory. However, bi- and trimolecular layers have been found in many instances.

Classic examples of adsorption compounds are the insoluble oxy-hydrates or hydrates of the oxides of multivalent metals ($Fe_2O_3 \cdot aq$; $Al_2O_3 \cdot aq$; $ZrO_2 \cdot aq$, *etc.*), and the hydrates of acidic insoluble metal oxides ($WO_3 \cdot aq$; $Ta_2O_5 \cdot aq$; $Nb_2O_5 \cdot aq$, *etc.*). Further examples are the materials resulting from the binding of "water of imbibition" by silica gel, cellulose, starch, *etc.* This adsorbed water may make up as much as 30% of the "dry weight," without the product losing its dry appearance. Adsorption compounds also include the blue complex of iodine with starch or basic lanthanum acetate, and the brown complex of iodine with freshly precipitated magnesium hydroxide. Instances of adsorption compounds formed by precipitation of oppositely charged colloids are provided by the tannin precipitates of Ta_2O_5 and Nb_2O_5, the precipitation of hydrolyzable metal salts from acid solution by tannin, and the tannin precipitation of albumins. Numerous alkaloid precipitations, that sometimes result in precipitates of definite composition, should also be included in this category.

Color lakes make up a special class of adsorption compounds. They are produced by precipitating gelatinous hydrated oxides of Al, Fe, Cr, Sn, Ti, *etc.*, from solutions of acid dyes. The dyes of the polyhydroxyanthraquinone series are particularly effective. The oxides and hydrated oxides of certain divalent metals (Be, Mg, Zn, and Cu) also form color lakes. These colored complexes likewise result if preformed oxides and oxyhydrates are treated with alkaline solutions of the appropriate dyes. Sometimes colored lakes can be produced from organic compounds that have no dyestuff character. Consequently, the more general term "lake" is more appropriate than "color lake." It is quite remarkable that all organic components of lakes are so constituted that the formation of inner complex salts with the particular metals appears quite natural. Some inner complex salts of this type have been produced by preparative methods and actually isolated. The color of a lake almost always differs from that of the progenitor dye or its alkaline solution; it is usually more intense. There is no uniform agreement in the literature regarding the structural characterization of products called lakes. They are regarded by some as inner complex salts and by others as the products of an adsorption. The author believes that both views are applicable in the sense that adsorption of the lake-forming components (as molecule or ion) on the surface of the hydrated oxide always is the first stage, and then, because of the tendency of the lake-former to form inner complex salts, an actual superficial coating with the resulting inner complex salt may follow. This view is supported by the fact that in many other cases adsorption is the preliminary stage of the formation of a stoichiometrically defined compound. Furthermore, it is now generally agreed that when

crystals grow, the first step is the adsorption of like ions or molecules, which then are built into the lattice. A definition of color lakes and lakes that would conform most closely to the experimental findings, accordingly would be: Lakes are adsorption compounds between hydrated metal oxides and such organic compounds as are, because of their constitution, capable of forming inner complex salts, in virtue of which capability it is possible but not always necessary for the adsorption compound to change into an inner complex salt. Many lakes have great analytical importance. A series of modern tests and methods of determining metals are based on the formation of these systems. Such procedures are highly sensitive, and some of them are quite selective. (Compare Chapter X.)

The great variation in formation-tendency and stability are noteworthy in these adsorption processes. Many adsorptions on nongelatinous materials are reversible, i.e., the adsorbed material can be removed by washing with water. Other adsorptions are irreversible. The extent of adsorption on a solid phase can vary widely and may range, according to the materials involved, from the retention of mere traces to the formation of an adsorption compound. The latter are often quite stable and tend to be formed readily. Certain adsorption compounds, and particularly certain metal lakes, if once formed, are extremely stable and withstand hydrogen ion concentrations at which they cannot be formed. If it is remembered that stoichiometrically defined complex compounds exhibit an analogous difference in formation-tendency and stability, it is clear that, in this respect, there is no fundamental difference between stoichiometrically defined and undefined compounds.
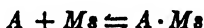
The Masking and Demasking of Reactions

MASKING

A reaction or, more correctly, a reaction system, is said to be masked if the normal course of a chemical change that leads to insoluble, or soluble colored or gaseous reaction products is prevented by the presence or addition of certain materials. For instance, some reactions of the mercuric ion do not occur after the addition of chlorides or cyanides, and certain reactions of the chloride ion, and almost all reactions of the cyanide ion (even the liberation of hydrogen cyanide by acids), are prevented if mercuric salts are added beforehand. The reason for these maskings is the slight ionic dissociation of $HgCl_2$ and $Hg(CN)_2$, formed by the union of Hg^{++} and Cl^- or CN^- ions, respectively. Masking of certain ions is accomplished far more frequently if suitable complex-formers are added. They produce new species of ions or molecules so rapidly and to such an extent that the original ion or molecule can no longer display its characteristic reactions because its concentration has been lowered too much.[1]

If the normal reacting material (molecule or ion) is designated as A, and the masking agent as Ms, every masking reaction can be represented by the general reversible equation:

$$A + Ms \rightleftharpoons A \cdot Ms$$

The position of the equilibrium of the masking reaction, *i.e.*, the decreased concentration of A, at equilibrium, determines the efficiency of masking. The reaction conforms to the law of mass action, and the equation shows that an excess of Ms favors the completeness of the masking.

The masking of reactions is a convenient and expedient device. Therefore, it is frequently and successfully applied to overcome difficulties encountered in the detection or the determination of materials in the presence of interfering substances showing analogous reactions. The selectivity of tests or methods of determination can sometimes be con-

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[1] Sometimes an excess of a reagent produces masking. Examples are the familiar solubility of certain hydrated oxides or hydroxides in excess caustic or ammonia, and the solubility of some heavy metal iodides or cyanides in excess alkali iodide or cyanide, respectively. These solubilities may be ascribed to the fact that the metal ion concentration derived from the newly formed compounds (alkali aluminate or double iodide, for instance) is less than that which corresponds to the solubility product of the hydroxide or iodide produced initially.

siderably heightened by this means.   On the other hand, the masking of reactions is also worthy of full consideration because the presence of masking agents may impair or prevent tests or methods that ordinarily can be used without hesitation.   Several characteristic kinds of reaction masking will be discussed here.

The reversible reaction[2]

$$2Fe^{+++} + 2I^- \rightleftharpoons 2Fe^{++} + I_2$$
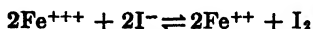
which is the basis of the iodimetric determination of iron, can be governed by suitably choosing conditions,[3] so that it proceeds quantitatively from left to right, at room temperature.   However, the reverse reaction is also realizable and ferrous iron can be quantitatively oxidized to the ferric state by iodine, if the resultant ferric ions are immediately removed or masked (sequestered) by incorporating them into a complex.   Sodium pyrophosphate is suitable for this purpose according to both Job[4] and Romijn,[5] or sodium potassium tartrate, according to Rupp.[6]   The presence of these compounds—as of all iron complex-formers[7]—prevents the oxidation of iodide ion to free iodine by ferric ion.   Consequently, it is then possible to titrate ferrous iron with iodine.

The reversible redox reaction $Fe^{++} - e \rightleftharpoons Fe^{+++}$ must be taken into account whenever ferrous salts are oxidized.   Accordingly, as was shown in the foregoing discussion of the iodimetric determination of iron, every oxidation of ferrous iron is facilitated and made more complete if the resulting ferric iron is masked and thus removed from the redox system.   This removal is the basis for the fact that the reducing action of ferrous salts is strengthened markedly in the presence of fluoride or phosphate ions, which readily form complexes with ferric iron.   Likewise, the oxidation of ferrous salts on exposure to air is much greater if fluorides are present.   This fact has practical significance.   For instance, the ferrous iron content of rocks after they have been reacted with hydrofluoric acid is usually determined by titration with potassium permanganate, or the presence of divalent iron is qualitatively indicated by the Prussian blue reaction.   The enhanced sensitivity of ferrous salts to air in the presence of fluorides causes serious errors here.   This interference

[2] A compilation of the literature is given by I. KOLTHOFF, Volumetric Analysis, Vol. 2, p. 422, New York, 1929.

[3] The iron must be present as the salt of a strong mineral acid, the H^+ concentration must be at least 1×10^{-1}, and a large excess of iodide ion is necessary.   See F. HAHN and H. CLOS, Z. anal. Chem. **79**, 26 (1929).

[4] A. JOB, Compt. rend. **127**, 59 (1898).

[5] G. ROMIJN, Pharm. Weekblad. **48**, 996 (1911); Chem. Ztg. **35**, 1300 (1911).

[6] E. RUPP, Ber. **36**, 164 (1903).

[7] L. V. SZEBELLÉDY, Z. anal. Chem. **81**, 26 (1930).

is patently connected with the ready formation of $[FeF_6]^{---}$ and the consequent raising of the reduction potential of ferrous solutions.[8] According to Barnebey,[9] this difficulty can be completely eliminated by the addition of boric acid; it binds the fluoride ions by forming complex boron-fluorine compounds. Ferrous salts are more stable toward air in the presence of fluorides and excess boric acid. The detection of ferrous iron or its titration with potassium permanganate then presents no difficulties. It is pertinent to point out that it is also possible to achieve stabilization by masking ferrous ions. This can be accomplished by the addition of α,α'-dipyridyl or α,α'-phenanthroline to ferrous solutions (see p. 319). The resulting $[Fe(\alpha,\alpha'\text{-dip})_3]^{++}$ and $[Fe(\alpha,\alpha'\text{-phen})_3]^{++}$ ions are stable in acid, neutral, and alkaline solution. The ferrous iron when incorporated in these complex cations is masked (protected) against oxidation by the air and moderately strong oxidizing agents.[9a]

An interesting example of masking an oxidation with resultant stabilization of a lower valence state of a metal was provided by Gleu.[10] Iodine normally oxidizes Ti^{+++} to Ti^{++++} with ease, but the reaction does not occur if ammonium fluoride is present. Doubtless, stable complex $[TiF_6]^{---}$ ions are formed.

The influence of masking is also exhibited in another useful redox reaction. The reversible reaction:

$$As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4H^+ + 4I^-$$
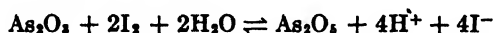
commonly used in the determination of arsenic, proceeds quantitatively from left to right only in alkaline bicarbonate or acetic acid solution, i.e., in a limited pH range. Rosenheim and Wolf[11] showed that the complete oxidation of arsenious acid by iodine in alkaline bicarbonate solution is prevented in the presence of considerable quantities of tungstate. This masking is obviously due to the formation of a complex compound of As_2O_3 and WO_3, in which the As_2O_3 is not oxidizable. In contrast, As_2O_3 can be oxidized extensively by iodine, and even in mineral acid solution, if the iodide ion, formed as shown in the preceding equation, is sequestered by masking. The addition of excess mercuric chloride accomplishes this. The iodide ion is converted into $[HgI_4]^{--}$ ion, and this shifts to the right the equilibrium which normally, in strong acid solution, lies far to the left. Here too, as in the regulation of the

[8] R. PETERS, Z. physik. Chem. 26, 193 (1898).

[9] O. BARNEBEY, J. Am. Chem. Soc. 37, 1481 (1915).

[9a] K. P. CARAWAY and R. E. OESPER, J. Chem. Education 24, 235 (1947) found ferrous ethylenediamine sulfate to be extraordinarily stable in the presence of air because the iron is part of a chelate ring.

[10] K. GLEU, Ber. 61, 707 (1928).

[11] A. ROSENHEIM and O. WOLF, Z. anorg. allgem. Chem. 193, 64 (1930).

redox reaction $Fe^{+++} \rightleftharpoons Fe^{++}$, it can be seen that a reagent which hinders or prevents a reaction may be utilized to force to practical completion an analytical reaction that normally proceeds only to equilibrium.

Masking is revealed most frequently by the impairment or complete prevention of precipitation and color reactions. The precipitation of certain metals, especially those of Group III of the qualitative scheme, as hydrated oxides and carbonates does not occur in the presence of nonvolatile organic compounds, particularly hydroxy acids and higher alcohols, such as Rochelle salt and citrates, glycerol, mannitol, *etc.* The chemistry of this masking of the precipitation of hydrous oxides is discussed on p. 91.

According to Curtmann and Dubin[12], 50 ml. of a solution containing 50 mg. of tartaric acid, on the addition of ammonia, produces no precipitate unless at least 20 mg. aluminum, 55 mg. iron, or 70 mg. chromium are present. In the presence of 50 mg. citric acid in 50 ml. of the test solution, precipitation of the hydrated oxide, on the addition of ammonia, begins only if at least 40 mg. aluminum, 70 mg. iron, or 90 mg. chromium are present. Accordingly, citric acid is a better masking agent than tartaric acid for preventing the precipitation of these elements as hydrous oxides. This is also shown by the fact that the precipitation of aluminum by sodium phosphate is hindered by citric, but not by tartaric acid.

The studies of Moser[13] are notable. He showed that organic compounds which contain one hydroxyl and one carboxyl group often become capable of forming complex ions only after a third acidic group is introduced. An example is the behavior of salicylic and sulphosalicylic acids toward ions of the ammonium sulfide group. Sulphosalicylic acid is an excellent complex-former for ferric, aluminum, and titanium ions, with which it produces soluble complex compounds of different stabilities. Iron sulfide alone is precipitated by hydrogen sulfide from an ammoniacal solution containing sulphosalicylic acid. On boiling, the titanium separates as $TiO_2 \cdot aq$, while the complexly bound aluminum remains unaltered. The complex compounds of these three metals with sulphosalicylic acid are stable toward alkali phosphate, whereas the corresponding manganese and magnesium salts are precipitated quantitatively. This is an instance of the graded activity of a masking agent, by means of which graduated, *i.e.*, selective, action of a precipitant is achieved. Jílek and Kota[14] found an interesting specific precipitation which can be accomplished by means of suitable masking and precipitating agents. Be^{++} ions are masked against hydroxide precipitation in ammoniacal

[12] L. Curtmann and H. Dubin, *J. Am. Chem. Soc.* **34**, 1485 (1912).

[13] L. Moser, *Monatsh.* **53–54**, 44 (1929).

[14] A. Jílek and J. Kota, *Z. anal. Chem.* **87**, 422 (1932); **89**, 345 (1932).

tartrated solutions of beryllium salts. Nevertheless, the addition of guanidine carbonate to such solutions produces a quantitative precipitation of the beryllium, the precipitate probably consisting of basic beryllium carbonate mixed with guanidine carbonate. Since other metal ions masked by tartrate do not react with guanidine carbonate, elegant separations of beryllium from aluminum, iron, uranium, thorium, zirconium, *etc.*, have been based on this differential behavior.

An example of autocomplex formation that can be observed easily and that leads to the partial prevention of precipitations, is furnished by chromium salts. The violet chromic solutions contain the hexaquo cation $[Cr(H_2O)_6]^{+++}$. These solutions are not stable on heating; acid radicals enter into the cation in place of the water molecules, with consequent change of color of the solution toward green. In the presence of sulfate ions, this leads to the formation of sulphato-chromic ions such as $[Cr(SO_4)_2(H_2O)_2]^-$ which are stable, and consequently contain sulfate groups that are not precipitable by barium chloride or benzidine. Hence sulfate cannot be determined in the normal manner in solutions of chromic salts. Preliminary removal of the chromium by precipitation as hydroxide, or binding it in a complex as acetate (see p. 33) is necessary. An analogous instance of automasking is provided by chromic chloride (see p. 31).

Ferric and aluminum ions will similarly partially mask sulfate radicals; they form metallosulfuric acids of the general formula $H[Me(SO_4)_2]$. The consequence is an incomplete precipitation of barium sulfate or, especially if ferric iron is present, precipitation of iron-bearing barium sulfate.[15] Therefore, the presence of ferric salts in sulfate determinations necessitates a preliminary precipitation or reduction of the iron. The formation of an iron-sulfuric acid is plainly indicated by the fact that the detection of sulfate ion by precipitation as $BaSO_4$ is considerably less sensitive in the presence of ferric salts. According to Hahn,[16] the respective quantities of sulfate that, under the same conditions, can be detected in the presence and absence of ferric iron equivalent to 0.4-0.8 g. ferric oxide are in the ratio of 1:5. The original sensitivity can be restored by reducing the ferric iron with hydrazine or hydroxylamine because ferrous compounds do not form iron-sulfuric acid. The incomplete precipitation of $BaSO_4$ from sulfuric acid solutions containing ferric or aluminum ions is due to a partial mask-

[15] Many materials are coprecipitated with $BaSO_4$ from true and colloidal solutions. This result can be ascribed to the particularly great adsorptive ability of $BaSO_4$. Experiments and the literature on this characteristic are given by H. B. Weiser in his essay "Adsorption by Precipitates" in Colloid Chemistry, Theoretical and Applied (edited by J. Alexander), Vol. 1, p. 600, New York, 1926.

[16] F. Hahn, *Ber.* **56**, 1733 (1923).

ing of the SO_4^{--} ions. This condition is relieved when the iron or aluminum is precipitated as hydrous oxide. A complex metallosulfuric acid in which the metal is masked against precipitants is formed with zirconium. The masking is revealed by the behavior of oxalic acid toward zirconium salt solutions that contain no SO_4^{--} ions as contrasted with the action of those in which such ions are present. The zirconium is precipitated quantitatively as oxalate from the former solutions, whereas the precipitation of zirconium fails completely, or in part, from solutions containing SO_4^{--} ions, depending on the quantity of sulfate present. According to Ruer[17] this masking of the oxalate precipitation is due to the formation of zirconyl sulfuric acid, *i.e.*, to the formation of $[ZrO(SO_4)_2]^{--}$ ions. This is also the reason why zirconium can be precipitated as basic sulfite from solutions containing hydrochloric acid, but not from solutions containing sulfuric acid.[18] Other zirconium reactions are similarly affected. For instance, Berg and Teitelbaum[19] recommended the quantitative determination of zirconium by precipitation with selenious acid. This procedure cannot be used if much sulfate ion is present. Likewise, titanium salts are masked against precipitation by selenious acid from solutions containing sulfuric acid; complex titanium-sulfuric acids are formed.[20]

It is characteristic of chromium that with acetic acid and acetates it readily produces complex salts derived from extremely stable polynuclear compounds. These are formed by merely boiling chromic solutions with alkali acetates. Under these conditions ferric and aluminum solutions precipitate hydrated oxides or basic salts, whereas chromic solutions remain perfectly clear and produce no precipitate even on the addition of alkali phosphate.[21] This fact was used by v. Knorre[22] to release the cationically masked sulfate groups in the green complex chromic sulfate solutions, so that they can be quantitatively precipitated as benzidine sulfate. The sulfate precipitation by means of barium chloride is likewise complete if the green chromic solutions have been boiled beforehand with sodium acetate. The masking of chromium by

[17] R. RUER, *Z. anorg. allgem. Chem.* **42**, 87 (1913).

[18] F. P. VENABLE and C. BASKERVILLE, *J. Am. Chem. Soc.* **17**, 448 (1895).

[19] R. BERG and M. TEITELBAUM, *Z. anorg. allgem. Chem.* **198**, 101 (1930).

[20] Compare S. G. SIMPSON and W. C. SCHUMB, *J. Am. Chem. Soc.* **53**, 921 (1931).

[21] B. REINITZER, *Monatsh.* **3**, 249 (1882). The precipitation of ferric and aluminum salts by alkali acetates is also partially prevented if chromic salts are present. Z. KARAOGLANOV and B. SAGORTSCHEV [*Kolloid-Z.* **72**, 291 (1935)] showed that these precipitates then contain chromium. They believe that colloid systems are produced as a result of typical induced precipitation and solution reactions, whose extent is determined by the ratio Fe:Cr, the dilution, the pH of the solution, the quantity of acetate, and the presence of other electrolytes.

[22] G. v. KNORRE, *Z. anal. Chem.* **49**, 478 (1910).

acetate is shown quite plainly in its behavior toward potassium chromate.[23] Chromic salts produce a brown precipitate of chromic chromate on heating with chromates. This precipitation is prevented completely if the chromic solution is boiled previously with sodium acetate, because the resulting chromacetic acid does not react with chromate.

Extremely interesting and quite unexpected masking effects by means of sodium triphosphate have been observed by Neuberg and his coworkers.[24] Since their findings were published in a rather inaccessible journal, in connection with important biological effects (specific enzymatic behavior of triphosphate), it seems advisable to go into considerable detail here. Sodium triphosphate, $Na_5P_3O_{10} \cdot 6H_2O$, is a salt of triphosphoric acid. This acid can be viewed either as an anhydride linking of three molecules of H_3PO_4 and thus represented by the formula

$$\begin{array}{ccccc}
HO & & OH & & OH \\
\diagdown & & | & & \diagup \\
& P{-}O{-}P{-}O{-}P & & \\
\diagup \parallel & & \parallel & & \parallel \diagdown \\
HO \quad O & & O & & O \quad OH
\end{array}$$
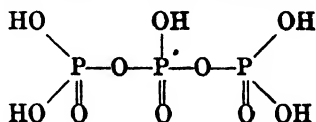
or as an isopolyacid of the true (hypothetical) ortho form of phosphoric acid and represented by the formula $P(OH)_5 \cdot P_2O_5$. In contrast to the free acid, the alkali triphosphates are stable and isolable.[25]

Sodium triphosphate differs in characteristic fashion from the familiar trisodium phosphate, Na_3PO_4. Whereas the latter is a precipitant for numerous metal ions, sodium triphosphate either produces no precipitate, or the initial precipitate dissolves smoothly in an excess of the reagent. This behavior has been demonstrated by trials with aqueous solutions of LiCl, $BeCl_2$, $MgSO_4$, $CaCl_2$, $Sr(NO_3)_2$, $BaCl_2$, $ZnSO_4$, $CdCl_2$, $FeSO_4$, $FeCl_3$, $CoCl_2$, $NiSO_4$, $MnSO_4$, $CuSO_4$, $Pb(NO_3)_2$, $VOSO_4$, $Al(NO_3)_3$, YBr_3, $In(NO_3)_3$, $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $AgNO_3$, $HgNO_3$, $TiOSO_4$, $Zr(NO_3)_4$, $SmCl_3$, $HCOOTl$, $Bi(NO_3)_3$, $SnCl_2$, $SnCl_4$, $Th(NO_3)_4$, and $UO_2(NO_2)_2$. Alkali hydroxide, phosphate, carbonate, borate, or ammonia produce no precipitate in triphosphate solutions of the foregoing metal ions. The addition of triphosphate to suspensions of these hydroxides, carbonates, etc., results in their immediate or rapid solution. Calcium is not precipitated by potassium fluoride, sodium oxalate, citrate, or mesotartrate if sodium triphosphate is also present. Freshly precipitated calcium fluoride, tartrate, or citrate are easily soluble in triphosphate solution. Freshly prepared Prussian blue and Turnbull's blue

[23] B. Reinitzer and P. Conrath, Z. anal Chem. 68, 81 (1926).

[24] C. N. Neuberg, L. Frankenthal and J. S. Roberts, Exptl. Med. Surg. 1, 386 (1943).

[25] Compare H. Huber, Z. anorg. Chem. 230, 123 (1936) regarding the preparation of these salts.

dissolve in triphosphate to form a cornflower blue solution, which gradually changes to violet and finally becomes colorless. Likewise, Williamson's violet, $KFe[Fe(CN)_6]$, and Hatchett's brown, $Cu_2[Fe(CN)_6]$, produce yellowish solutions. Insoluble uranium red ($U_6S_2H_6O_{16} = 2UO_3S \cdot 3H_2UO_4$) forms an olive-green solution. Obviously, these iron, copper, and uranium compounds combine with triphosphate to form complex compounds. A precipitate of uranyl ferrocyanide produces a pale yellow solution on the addition of triphosphate. In contrast to normal uranyl phosphate, which is insoluble in acetic acid, a triphosphated uranyl solution remains clear, even though an excess of acetic acid is introduced. Addition of triphosphate discharges the violet color of ferric salicylate and sulfosalicylate solutions; they become almost colorless. The precipitation of the fluorides of Ca, Sr, Ba, Mg, and Pb is hindered or prevented by triphosphate. Lead fluoride dissolves easily in triphosphate, and, if the lead concentration is low, neither the orthophosphate or chromate will precipitate. Freshly prepared $PbCrO_4$ and $PbSO_4$ dissolve in a sufficient quantity of triphosphate. The addition of K_2SO_4 or K_2CrO_4 to a solution of $Pb(NO_3)_2$ containing triphosphate gives no precipitate, but free H_2SO_4 and $K_2Cr_2O_7$ react as usual. The same reaction conditions hold for $PbSO_3$. Likewise, only free H_2SO_4 or warm $K_2Cr_2O_7$ produce precipitates in triphosphated solutions of $BaCl_2$, whereas K_2SO_4, Na_2SO_3, or K_2CrO_4 are without effect. $BaSiF_6$ is only slightly soluble in triphosphate. The solution of CaF_2 in triphosphate is stable for days; the Ca^{++} ion can be detected by means of oxalate only after destruction of the triphosphate complex by boiling with acids. The following compounds, when freshly precipitated, are soluble in cold triphosphate, or after slight warming: Ag molybdate and tungstate; Pb myristate, palmitate, stearate; Cu_2I_2 (yellow-green solution); PbI_2, HgI_2, BiOI (colorless solutions). The solution containing $PbI_2\text{-}Na_5P_3O_{10}$, on the addition of a large quantity of Na_2HPO_4 becomes turbid, due to the precipitation of $Pb_3(PO_4)_2$, whereas the corresponding bismuth solution is stable against orthophosphates. An ordinary solution of bismuth-potassium iodide forms a precipitate of $BiPO_4$ when Na_2HPO_4 is introduced, while even an excess of triphosphate has no precipitating action. Silver chromate is soluble in triphosphate, likewise yellow lead metavanadate produces a colorless solution. Triphosphates hinder or prevent the precipitation by potassium chromate of mercuric (but not mercurous) salts. The precipitation of metatitanic acid by boiling titanic sulfate with sodium acetate does not take place if triphosphate is present.

The foregoing observations by Neuberg and his co-workers show that sodium triphosphate is far more effective in masking inorganic precipita-

tion reactions than any hitherto known inorganic or organic masking agent. With few exceptions (see p. 74), sulfide precipitations are not masked by triphosphate. Consequently, it is reasonable to expect that those organic color and precipitation reagents which lead to compounds whose ion products are approximately as low as those of the sulfides will maintain their activity in the presence of triphosphate. Accordingly, there are interesting possible applications of sodium triphosphate in analytical chemistry. It must be emphasized that triphosphate functions as a masking agent only in neutral or alkaline solutions. In the presence of acid, the unstable triphosphoric acid breaks down with restoration of the normal reactivity of the masked metals (see p. 104 concerning demasking). The composition of the soluble heavy metal compounds of triphosphoric acid is not known; probably, the masked metal is incorporated in a complex anion.

The influence that certain masking agents may exert on reversible redox reactions has been pointed out on p. 68. Masking agents can also affect irreversible redox reactions. For example, $PdCl_2$ solutions, which are quite easily reduced to free palladium by carbon monoxide or alkali formate, remain completely unaltered, even at the boiling temperature, if sodium thiosulfate is also present.[26] The concentration of Pd^{++} ions is so greatly reduced through the formation of $[Pd(S_2O_3)_2]^{--}$ ions, that a masking against the foregoing strong reducing agents results.

Instances of masking of irreversible redox reactions also include those in which certain materials that ordinarily are oxidized very easily by potassium permanganate are protected against this strong oxidizing agent if they are made into complex compounds. Sodium sulfite normally is oxidized instantaneously to sulfate by potassium permanganate, but in the presence of an excess of mercuric salts it remains unoxidized for a long time at room temperature, or even if warmed gently. The reason is that SO_3^{--} ion is no longer present, but in its stead the ion of the stable sodium sulphitomercuriate, $Na_2[Hg(SO_3)_2]$.[27] In fact, oxalic acid, the usual primary standard for potassium permanganate, is quite stable against this oxidant in sulfuric acid solution, even on warming, if considerable quantities of molybdic acid are present.[28] Patently, molybdenooxalic acids such as $MoO_3 \cdot H_2C_2O_4$ or $2MoO_3 \cdot H_2C_2O_4$, described by Rosenheim,[29] and Weinland,[30] are responsible for this masking of oxalic

[26] W. DALLER, *Z. anal. Chem.* **103**, 87 (1935–36).

[27] This masking probably involves not only a complex salt of this type, but also an equilibrium with a sodium salt of mercury sulfonic acid $Hg:(SO_2ONa)_2$. Compare O. RUFF and E. KROHNERT, *Z. anorg. allgem. Chem.* **114**, 203 (1920).

[28] F. FEIGL, *Z. anal. Chem.* **74**, 391 (1928).

[29] A. ROSENHEIM, *Z. anorg. allgem. Chem.* **4**, 352 (1893); **34**, 427 (1905).

[30] R. WEINLAND, *Z. anorg. allgem. Chem.* **108**, 243 (1919).

acid against permanganate. The consumption of potassium permanganate cannot exceed that which is equivalent to the free oxalic acid provided by the equilibrium system:

$$H_2[MoO_3 \cdot C_2O_4] \text{ or } MoO_3 \cdot H_2C_2O_4 \rightleftharpoons MoO_3 + H_2C_2O_4$$
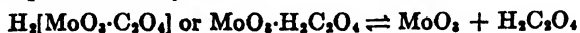
However, this amount of oxalic acid is smaller when larger quantities of molybdic acid are present since, in accordance with the law of mass action, the equilibrium is shifted toward the side of the non-oxidizable molybdenooxalic acid. In fact, in the presence of 5 to 10 times its weight of molybdate, oxalic acid is so stabilized against permanganate that this reaction fails, although normally, if no other oxidizable materials are present, this redox reaction is an unequivocal test for oxalic acid.

The presence of molybdate also masks the reaction of oxalate ion with calcium ion. In acetic acid solution, the usual precipitation of calcium oxalate is prevented completely if enough molybdate is present. The same also holds for solutions of complex chromic and ferric oxalates, whose oxalate ion concentration is not sufficient to exceed the solubility product of calcium oxalate.

The formation of these molybdenooxalic acids is also the reason why not only the sulfide precipitation of molybdenum[31] but also the familiar delicate test for phosphate with ammonium molybdate are impaired in the presence of considerable quantities of oxalic acid.[32] In the latter case, when the molybdate is added it is bound into molybdenum-oxalic acid. Accordingly, no yellow precipitate of $(NH_4)_3PO_4 \cdot 12MoO_3$ will be formed until all of the oxalic acid has combined with the molybdic acid; a further excess of molybdate must be available to precipitate phosphate. The formation of molybdenooxalic acid is also responsible for the ease with which ammonium or potassium phosphomolybdate dissolves in warm, dilute oxalic acid. This effect is remarkable in view of the stability of these compounds toward strong mineral acids. A partial or complete prevention of the precipitation of ammonium phosphomolybdate can also be brought about by masking the phosphate ion. This has been demonstrated by Cohen[33] and Oberhauser.[34]

Metallic antimony is dissolved to only a slight extent by nitric acid; it is oxidized chiefly to $(Sb_2O_5)_n \cdot xH_2O$. However, in the presence of tartaric and other organic hydroxy acids, clear solutions are obtained; they contain complex trivalent and quinquevalent antimony compounds. Likewise, metallic tin normally is converted into insoluble metastannic acid by nitric acid, but it can be brought into solution at low tempera-

[31] J. STERBA-BÖHM and J. VOSTŘEBAL, *Z. anorg. allgem. Chem.* **110**, 85 (1920).

[32] F. FEIGL, *Z. anal. Chem.* **74**, 389 (1928).

[33] L. COHEN, *J. Am. Chem. Soc.* **29**, 1194 (1907).

[34] F. OBERHAUSER, *Ber.* **60**, 38 (1927).

tures if tartaric or citric acid is also present. This solution is not stable, however; on warming, the stannic acid separates completely. Czerwek[35] made the remarkable observation that tin acts quite differently in the presence of antimony. If an antimony-tin alloy or mixture is treated at 40–50°C. with nitric and tartaric acids, a perfectly clear solution is quickly obtained which can be heated to boiling with no precipitation of stannic acid. He justly calls the process "induced solution" (see p. 147). This anomalous solubility is probably due to the formation of a complex compound containing antimony, tin, and tartaric acid, or to a protective colloid action exerted by the antimony-tartaric acid compound on the stannic acid, which normally coagulates. As the tin can be precipitated as phosphate from solutions produced in this way, it can be separated from the antimony by utilizing this abnormal solubility.

Interference with characteristic reactions of metal-acids as a consequence of complex formation is often encountered. An example was just given, namely, the prevention of certain reactions of phosphoric and oxalic acids due to the formation of molybdenooxalic acids. The ease with which such combinations are formed, together with their stability, is the cause of the non-occurence or the sluggishness of still other reactions that normally are shown by molybdic acid.[36] Thus Lecocq's[37] sensitive test for molybdenum by means of diphenylcarbohydrazide, (formation of a red-violet coloration or precipitate) does not function in the presence of oxalic acid if the ratio $MoO_3:H_2C_2O_4 = 1:1$ is reached or exceeded. The sensitive color reactions for molybdate with alkali thiocyanates,[38] pyrocatechol, pyrogallol, tannic acid[39] and phenylhydrazine[40] are prevented by the presence of oxalic acid. Likewise, potassium ferrocyanide, hexamethylenetetramine, or aromatic amines, produce no precipitates when added to acid molybdate solutions containing excess oxalic acid.

Quite remarkably, many reactions of the molybdate ion in acid solution are masked if hydrogen peroxide is present. This effect involves the formation of permolybdic acid, H_2MoO_5, whose MoO_5^{--} anions do not have the precipitating capability of MoO_4^{--} ions. For instance, if hydrogen peroxide is present in acetic acid solution, molybdate is not precipitated by Ba^{++}, Pb^{++}, Hg^{++}, or Ag^+ ions, or by benzoinoxime or methylene blue. Furthermore, the color reaction between molybdate and diphenylcarbazide in sulfuric acid solution does not occur when hydrogen peroxide

[35] A. Czerwek, Z. anal. Chem. 45, 505 (1906).
[36] Compare F. Feigl, Z. anal. Chem. 74, 390 (1928).
[37] E. Lecocq, Bull. assoc. belg. chim. 17, 412 (1903).
[38] W. Ellram, Chem. Ztg. 20, Rep. 153 (1896).
[39] J. Stahl, Ber. 25, 1600 (1892).
[40] L. Spiegel and T. Maass, Ber. 36, 512 (1903).

is present.[41]   It seems, therefore, that hydrogen peroxide can, in general mask the reactions of the MoO_4^{--} ion because of the production of permolybdate.   Tungstic acid or WO_4^{--} ions likewise form with hydrogen peroxide a per- compound whose constitution is analogous to that of permolybdic acid.   Consequently, it has been found that the precipitation of heavy metal tungstates (Ba, Pb, *etc.*) is also prevented by hydrogen peroxide.   In contrast, the precipitation reactions of vanadic acid are not masked by hydrogen peroxide, despite the formation of per- compounds. This finding doubtless is based on the fact that the per- compounds of quinquevalent vanadium, according to Meyer and Pawletta,[42] contain the

grouping $\displaystyle \mathord{\to}V{<}{\begin{smallmatrix}O\\ \ \\ O\end{smallmatrix}}$, and hence are constituted quite differently from the

per- compounds of hexavalent tungsten and molybdenum, in which the acidic group —O—OH is present.   The behavior of the per- compounds of molybdenum, tungsten, and vanadium clearly exhibits the importance of certain atomic groupings in determining the occurrence or prevention of precipitation reactions.   Such effects, which are of vital significance to specific and selective actions, will be discussed in detail in Chapter VI.

It is entirely in line with the masking of the precipitation reactions of MoO_4^{--} and WO_4^{--} ions by hydrogen peroxide, that precipitated molybdates and tungstates are quantitatively soluble in acetic acid + hydrogen peroxide.   Warming is sometimes necessary.   Lead molybdate presents a remarkable exception, as it is completely resistant to this solvent mixture.[41]   The fact that the precipitation of lead molybdate is prevented by hydrogen peroxide, whereas the precipitated salt is insoluble in this reagent, signifies that an equilibrium:

$$PbMoO_4 + H_2O_2 \rightleftharpoons Pb^{++} + MoO_5^{--} + H_2O$$
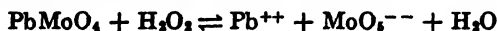
is established either not at all or only at an immeasurably low rate. Such false equilibria are almost universally encountered when precipitations do not occur under certain circumstances, whereas the product when once precipitated will not dissolve when exposed to the same conditions.   Very familiar instances of this are furnished by CoS and NiS in their behavior toward dilute acids (compare Chapter V).   The stability of precipitated lead molybdate far exceeds the stability of precipitated cobalt and nickel sulfide, because, even after prolonged boiling with acetic acid + hydrogen peroxide, not a trace of $PbMoO_4$ goes into solution.   The insolubility of this material may possibly be due to nondissociation of the slight amount of the $PbMoO_4$ that dissolves; in other words,

[41] F. Feigl and I. D. Raacke, *Anal. Chim. Acta.* **1**, 317 (1947).
[42] J. Meyer and A. Pawletta, *Z. anal. Chem.* **69**, 15 (1926).

it may remain, completely or for the most part, molecularly dissolved. If this be true, then the concentration of MoO_4^{--} ions requisite for the formation of MoO_5^{--} ions:

$$MoO_4^{--} + H_2O_2 \rightarrow MoO_5^{--} + H_2O$$
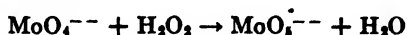
would not be attained. A salt that is soluble in water, but which does not ionize, is known as a *pseudo* salt. Solutions of *pseudo* salts frequently do not exhibit the expected ionic reactions; they are innately masked. Accordingly, it seems not too far out of the way to regard lead molybdate, in contrast to other slightly soluble molybdates, as being present in its water solutions as a nondissociating *pseudo* salt.

The detection and determination of phosphate by means of ammonium molybdate is not successful in a solution that contains hydrogen peroxide. The permolybdic acid that is formed furnishes too little MoO_4^{--} to exceed the solubility product of the $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot aq$ which should precipitate. It is interesting that this compound behaves as lead molybdate does toward hydrogen peroxide. As already stated, ammonium phosphomolybdate does not form in a solution containing large amounts of hydrogen peroxide, but nevertheless the solid, when produced under normal conditions, is entirely stable against hydrogen peroxide. Other insoluble salts of phosphomolybdic acid behave in the same way.

As might be expected, free phosphomolybdic acid is likewise decomposed by hydrogen peroxide with production of permolybdic acid. If this decomposition is carried out in the presence of salts of potassium, ammonium, rubidium, or cesium, which are known to be precipitable by phosphomolybdic acid, only cesium phosphomolybdate will come down if the alkali salt solution, which contains acetic acid and hydrogen peroxide, is treated dropwise with a 10% solution of the precipitant. The explanation probably lies in the fact that, in this case, the rate of precipitation, which depends not only on low solubility but also on specific factors of the rate of nuclei formation and crystal growth (see Chapter XI), exceeds the velocity of the masking reaction between phosphomolybdic acid and hydrogen peroxide. This makes possible a specific test for cesium within the alkali and alkali earth metal groups.[42a]

Hydrogen peroxide also causes reaction masking in acidified solutions of titanium salts because of the production of soluble red-brown peroxotitanic acid compounds. For instance, peroxotitanylsulfuric acid,[43] $H_2TiO_2(SO_4)_2$, whose color makes possible accurate colorimetric determinations of titanium, is formed in solutions containing sulfuric acid. When hydrogen peroxide is present in acidified titanic solutions, the

[42a] F. FEIGL and I. D. RAACKE, unpublished studies.
[43] Compare R. SCHWARZ, *Z. anorg. allgem. Chem.* **210**, 303 (1933).

anion $[(TiO_2)X_4]^{--}$ (X = univalent acid radical) is produced, and accordingly the concentration of Ti^{++++} ions is lowered so greatly that precipitation with phosphate ion is no longer feasible. Lundell and Knowles[44] used this fact as the basis of separating zirconium and titanium, since zirconium can be quantitatively precipitated as $Zr(HPO_4)_2$ despite the presence of hydrogen peroxide. If the acidified solutions of peroxotitanic acido compounds are alkalized with ammonia or alkaline hydroxide (carbonate), the color disappears, but no precipitation of $Ti(OH)_4$ ensues, i.e., the masking persists. Probably the reaction:

$$\left[\left({O \atop O}{\Large >}Ti\right)X_4\right]^{--} + 4\,OH^- \rightarrow 4X^- + 2H_2O + \left[{O \atop O}{\Large >}Ti{\Large <}{O \atop O}\right]^{--}$$
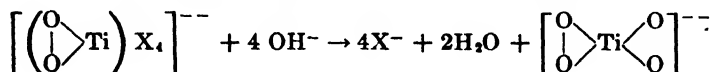
occurs. In other words, alkali salts of peroxoorthotitanic acid[45] are produced and their solutions are fairly stable at room temperature and in the presence of excess hydrogen peroxide. Faber,[46] who was the first to make careful experimental studies of the systems containing titanium salts and hydrogen peroxide, had noted the failure of ammonia to produce a precipitate. However, this masking of the precipitation of $Ti(OH)_4$ was not applied in the separation of titanium from iron and aluminum in gravimetric procedures until quite recently.[47] The addition of hydrogen peroxide to solutions of zirconium and thorium salts likewise results in the production of per- compounds. Nevertheless, the author has found that the hydroxide precipitation of these metals from peroxide-containing solutions is not impaired, a finding that has analytical possibilities. In this connection, it should also be noted[41] that $Ti(OH)_4$ can be precipitated by treating basic hydrogen peroxide-titanium solutions with alkali sulfite or nitrite, or with formaldehyde or hexamethylenetetramine, i.e., with reagents oxidizable by hydrogen peroxide. Likewise, the normal precipitability of MoO_4^{--} and WO_4^{--} ions is restored on adding nitrite or formaldehyde to acidified molybdate or tungstate solutions, which have been masked by hydrogen peroxide. Consequently, the masking is reversed, i.e., demasking occurs. This process will be discussed in later sections of this chapter.

Among color reactions that can be masked, the ferric thiocyanate

[44] G. E. LUNDELL and H. B. KNOWLES, *J. Am. Chem. Soc.* **41,** 1801 (1919).

[45] No statements regarding this color-discharging reaction could be found in the literature, which deals almost entirely with the H_2O_2 reactions of titanium in acid solution. The postulate of the author, that a peroxoorthotitanic acid is formed, is supported by the fact that a yellow precipitate is produced at once when thallium salts are added to ammoniacal peroxide-titanium solutions. The precipitate could be a thallium salt of peroxoorthotitanic acid.

[46] P. FABER, *Z. anal. Chem.* **46,** 287 (1907).

[47] A. GUERREIRA, Rio de Janeiro, private communication.

reaction will be cited.   It does not occur, or the color is discharged, if sufficient alkali fluoride or phosphate is present or is added to the acid test solution; complex $[FeF_6]^{---}$ or $[Fe(PO_4)_2]^{---}$ ions are formed, and the concentration of ferric ion is no longer adequate to exceed the ion product of the ferric thiocyanate.[48]   (Tartaric and citric acid act similarly.)   This fact must be considered when testing for iron and can, if necessary, also be used to prevent the interference by ferric salts in the detection of cobalt by the thiocyanate reaction.   Likewise, the color reaction in dilute solution between zirconium salts and alizarin (formation of red zirconium alizarinate) does not occur, or can be made to disappear, if fluorides are present or added, because soluble, colorless complex $[ZrF_6]^{--}$ ion is then formed.   de Boer developed a very sensitive and selective test for fluoride, based on this masking reaction.[49]

The interference with precipitation reactions by a complex-former becomes more complete the greater the solubility product of the compound to be precipitated, and the greater the excess of complex-former added.   The same holds for the impairment of color reactions.   Since its solubility limits the quantity of masking agent that can be added, the difference in the ion products of the compound to be masked and of the compound produced by the masking will always be decisive for the interference with the formation of a precipitate.   This is the reason why sulfide precipitations which, as a rule, result in solids with low solubility products, are masked much less frequently than other precipitation or color reactions.   For instance, the precipitation of iron as hydrated oxide is easily and completely prevented by the addition of organic nonvolatile hydroxy compounds, but not its precipitation as iron sulfide.

There are, however, masking agents for sulfide precipitations.   It is well-known that ammonium sulfide produces no precipitate from neutral or ammoniacal copper solutions after they have been decolorized with potassium cyanide, and freshly precipitated copper sulfide is completely soluble in potassium cyanide.   The cause of the masking, and of the solubility of the copper sulfide, is the formation of $K_2[Cu_2(CN)_4]$.   The analogous cadmium compound, the soluble $K_2[Cd(CN)_4]$, is much less stable, and consequently alkali sulfide precipitates all the cadmium, as sulfide, from potassium cyanide solutions.   The difference in the

[48] B. RICCA and P. MEDURI [Gazz. chim. ital. 64, 235 (1934)] found that merely mixing equimolar quantities of $FeCl_3$ and H_3PO_4 causes decolorization, and the Fe^{+++} reaction with KCNS disappears.   At this ratio there is also a maximum conductivity compared with the original and final solutions.   These observations, as well as the isolation of a silver salt, indicate that in such solutions the presence of the compound $H_3[FeCl_3(PO_4)]$ or its ions must be taken into account.

[49] J. H. DE BOER, Chem. Weekbl. 21, 404 (1924).

stability of the copper and cadmium cyanide complexes is shown further by their different behavior toward formaldehyde.[50]   The sulfide precipitation of nickel also is prevented by potassium cyanide because of the formation of $K_2[Ni(CN)_4]$, while solutions of the analogous complex cyanides of zinc and manganese give the respective sulfides on addition of ammonium sulfide.

The precipitation of WO_3 and WS_3 does not occur from the soluble complex compound of tungstic acid and tartaric acid; this makes possible a convenient separation of molybdenum from tungsten.   The precipitation of WO_3 from solutions of tungstates by strong mineral acids can likewise be prevented by adding phosphoric acid, which forms complex tungsten phosphoric acids.

The strong tendency of quadrivalent tin to form stable complex compounds is shown by the fact that the precipitation of stannic sulfide can be prevented by considerable quantities of oxalic, phosphoric or hydrofluoric acids.[51]   This is in agreement with the solubility of precipitated stannic sulfide in these acids.   If, however, boric acid is added to a stannic solution that is masked against hydrogen sulfide by hydrofluoric acid, SnS_2 precipitates quantitatively because the formation of the complex anion $[BF_4]^-$ liberates the precipitable tin ion from the $[SnF_6]^{--}$ ion, which is less stable toward boric acid.[52]

The excellent method of Vortmann and Metzel[53] for separating antimony and tin is based on the masking of the precipitation of tin as sulfide and the absence of a corresponding effect on the formation of Sb_2S_5 in phosphoric acid solution.   Presumably, the sulfide precipitation of germanium, which greatly resembles tin, can also be prevented by the presence of these complex-forming acids.   Müller[54] has shown this is true for hydrofluoric acid, at least.   He found that, if the precipitation of GeS_2 is prevented by this acid, as little as 0.01% arsenic can be determined in germanium preparations.

Likewise, the precipitation of mercury as sulfide by hydrogen sulfide can be prevented if considerable quantities of iodide ion are present in acid solution,[55] because the mercuric ion is converted into the complex $[HgI_4]^{--}$ ion.   Addition of alkali cyanide to a neutral mercuric solution produces soluble, nondissociating $Hg(CN)_2$.   The precipitation of HgS is thus prevented.   Since HgS, with a solubility product of 2×10^{-49} — 4×10^{-51}, is the least soluble of all metal sulfides, this example demon-

[50] F. Feigl, Spot Tests, p. 76.
[51] W. McCay, J. Am. Chem. Soc. 31, 373 (1909).
[52] N. Furman, Ind. Eng. Chem. 15, 1071 (1923).
[53] G. Vortmann and A. Metzel, Z. anal. Chem. 44, 525 (1905).
[54] J. Müller, J. Am. Chem. Soc. 43, 2549 (1921).
[55] H. Wegelius and S. Kilpi, Z. anorg. allgem. Chem. 61, 413 (1909).

strates that there is no limit to the prevention of precipitation reactions, but that it is merely a matter of finding a suitable masking agent.

Although all the masking agents cited thus far have resulted in colorless products, it may not be concluded that this is a necessary condition. Color reactions may also serve for masking, as is shown by the use of α,α'-dipyridyl or of α,α'-phenanthroline for this purpose. These colorless bases react with ferrous salts in acid or neutral solution to produce deep red complex ions (cf. p. 319) that are stable toward even alkalies and alkali sulfides. According to Ferrari[56] the formation of the dipyridyl or phenanthroline compounds can be used to obviate the interference of iron in the precipitation of magnesium, beryllium, aluminium, and titanium.

The iron in the ferrous dipyridyl or phenanthroline compounds is a constituent of a colored complex cation. Ubaldini and Pelagatti[57] have shown that a color reaction, through which ferrous iron becomes a constituent of a complex anion, can likewise be masked. Thioglycolic acid forms stable red-violet $[Fe(S-CH_2COO)_2]^{--}$ ions in ammoniacal solution. Magnesium and beryllium can be precipitated quantitatively by phosphate, *etc.*, from such masked solutions, whereas these separations are obviously impossible if the iron is not masked. The two instances of the masking of ferrous iron demonstrate that the sense of the charge of the complex ion is not a significant factor, but the sole determinant is that formation of the complex must lower the Fe^{++} ion concentration to such an extent that the normal precipitation reactions cannot occur.

An intelligent application of masking agents·is of great practical importance with respect to the improvement of the specificity or selectivity of reagents and reactions. However, a general acquaintance with a particular masking agent is not a sure guarantee that the masking will really occur or that the use of this masking agent will not be attended by complications. The actual effectiveness depends far more on the other materials that may be present. Thus, ferric salts remain unchanged on the addition of sodium potassium tartrate, ammonia and dimethylglyoxime, while, under these conditions, cobalt salts give colored, soluble complex compounds. Nevertheless, if cobalt and ferric salts are both present, a red-brown precipitate containing iron and cobalt is formed.[58] Its composition is $FeCoC_{12}H_{19}N_2O_6$ (see p. 274).

A similar phenomenon that, like the previous case, involves a form of induced precipitation (see p. 147), was observed by Brukl and Maxymo-

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[56] C. Ferrari, *Ann. chim. appl.* **27**, 479 (1937); *Chem. Abstracts* **32**, 4901 (1939).

[57] T. Ubaldini and V. Pelagatti, *Chimica e industria* (*Milan*) **19**, 131 (1937).

[58] G. Weeldenburg, *Rec. trav. chim.* **43**, 465 (1924). See also O. Brunck, *Z. angew. Chem.* **27**, 375 (1914).

vicz[59] in the action of ammonia on a solution of a lead salt in the presence of tellurium and sulphosalicylic acid.   A precipitate containing both lead and tellurium is obtained, although solutions free of tellurium remain clear, and tellurium, when alone, is kept in solution by excess ammonia.

The behavior toward ammonia or alkali carbonate, of tantalum, niobium, and titanium (as oxalates), in the presence of arsenic acid or phenylarsinic acid, is quite impressive as regards the phenomenon of an induced precipitation from a masked solution.[60]   Tantalum, when unaccompanied, is immediately precipitated in the cold as Ta_2O_5, whereas niobium is masked completely and no Nb_2O_5 precipitates, even after prolonged boiling.   (In warm solutions, titanium behaves analogously to tantalum.)   Consequently, it was expected that this divergent behavior could be made the basis of a quantitative separation of tantalum and titanium from niobium.   This problem is exceedingly difficult and hitherto has been solved only in a very roundabout way.[61]   It was found, however, that in a mixture of tantalum and niobium, masking of tantalum, as well as of niobium, first occurred, and on prolonged boiling the hydrated oxides of both metals came down quantitatively.   Mixtures of titanium and niobium behaved quite analogously, and in this case also on boiling, the oxides precipitated together quantitatively.   In other words, the complex containing niobium was broken down with induced precipitation of Nb_2O_5.   These examples illustrate the important fact that undesirable impairment of the activity of masking agents by attendant materials should always be considered as a possibility in any analytical application of masking, and must be checked experimentally.

The general equation (see p. 67) representing the masking of reactions shows that the efficacy of a masking agent depends on the degree to which it lowers the concentration of one of the original ionic species by binding it into a complex.   A precipitation or color reaction is prevented, i.e., masked, only when the concentration of the original ionic species is decreased to such an extent that the ion concentration necessary for the visible formation of the particular soluble or insoluble resultant material is not exceeded.   It follows from this that when choosing a masking agent one should consider the minimal value of the ion product that will permit a positive response to a color or precipitation reaction. Even a feeble masking agent can prevent the production of a visible color or precipitate in the case of reactions which have a relatively large limiting

[59] A. Brukl and W. Maxymovicz, Z. anal. Chem. 68, 16 (1926).

[60] F. Feigl and C. Pinto, Unpublished studies on the separation of tantalum and niobium.

[61] Compare W. R. Schöller and A. R. Powell, The Analysis of Minerals and Ores of the Rarer Elements, 2nd Ed., p. 153, Edinburgh, 1940.

value of the particular ion product.   For example, the addition of glycerin to solutions of copper, cobalt, nickel, or zinc salts produces complex metal-glycerin cations, and the dropwise addition of base then results in no precipitation of hydroxide or basic salt. ˙Hence, according to Wagner,[62] any free mineral acid present in such solutions may be titrated with an accuracy sufficient for technical purposes if glycerin is added beforehand.   Phenolphthalein is used as indicator.   Hazel and Eglof[63] provided an interesting example of the value of a weak masking agent. Mannitol, like other sugars, dissolves alkaline earth hydroxides, and accordingly prevents their precipitation when bases are added to solutions of alkaline earth salts.   The resulting complex compounds[64] are quite unstable, as shown by the fact that CO_3^{--} ions throw down the corresponding alkaline earth carbonates when introduced into the alkaline sugar heated solutions.   Since the precipitation of $Mg(OH)_2$ is not prevented by mannitol, these workers precipitate the magnesium quantitatively as $Mg(OH)_2$ by adding alkali to an acid mannitol-containing solution of magnesium and calcium.   The solution thus freed of magnesium can then be acidified with acetic acid, and the calcium precipitated as oxalate.   In this manner, they avoid the well-known difficulty of the Ca-Mg separation that is encountered in the precipitation of calcium from an acetic acid solution by means of oxalate.   Ordinarily, coprecipitation of magnesium oxalate can be expected, especially if considerable quantities are present.

The entire preceding discussion of the masking of reactions makes it clear that a system masked against a certain reagent, despite the lowering of the concentration of the particular ionic system, is not necessarily masked against another but more sensitive reagent.   The precipitation and color reactions of ferric ions lend themselves well to a demonstration of this point.   A tartrated ferric solution, in which the iron is bound into a complex ferric tartrate, is completely masked against hydroxide precipitants.   Nevertheless, all the iron in a clear alkaline ferric tartrate solution can be precipitated by adding a soluble sulfide, because the solubility product of Fe_2S_3 is much smaller than the solubility product of $Fe(OH)_3$.   The familiar thiocyanate color reaction does not occur in phosphated ferric solutions.   The concentration of free Fe^{+++} ions is lowered so greatly by formation of complex $[Fe(PO_4)_2]^{---}$ ions that the ion concentration needed to form $Fe(CNS)_3$ is not attained.   On the other hand, acidified ferric solutions that have been masked against thiocyanate by phosphate still contain enough Fe^{+++} ions to give a blue color with the

[62] H. WAGNER, Z. anal. Chem. **95**, 311 (1933).

[63] W. M. HAZEL and W. K. EGLOF, Ind. Eng. Chem., Anal. Ed. **18**, 759 (1946).

[64] A. GRÜN, and J. HUSMANN, Ber. **43**, 1291 (1910); Monatsh. **37**, 205 (1916).

more sensitive reagent "ferron" (see p. 187). The fact that a masking agent does not prevent all reactions of a given ionic species is important in the achievement of appropriate maskings; it also is the basis of certain analytical procedures.

Masked reaction systems can be used as reagents. An excellent instance is provided by the ammoniacal solution of silver chloride. This liquid, which contains complex $[Ag(NH_3)_2]^+$ ions, is masked against Cl^- ions. The masking equilibrium:

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$
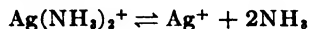
lies so far to the left that there are not sufficient Ag^+ ions to exceed the solubility product of AgCl when Cl^- ions are added. However, the concentration of Ag^+ ions is still high enough to exceed the solubility product of the less soluble silver halides. Consequently, AgBr or AgI can be precipitated if Br^- or I^- ions are added to the masked solution. Accordingly, an ammoniacal solution of silver chloride is a good reagent for detecting bromide or iodide in the presence of chloride.[65] For the same reason, an ammoniacal solution of AgBr can be used as a test for iodide.

The value of a masked reaction system as a reagent, is shown still better in the familiar Fehling's test for reducing sugars.[66] In this procedure, an alkaline tartrated cupric solution is warmed with the test solution, and even traces of reducing sugars are revealed by a red precipitate of Cu_2O. Fehling's solution contains complex copper tartrate anions and even though basic it obviously is masked against the precipitation of $Cu(OH)_2$. However, the instability of the complex ions is adequate to furnish enough unmasked Cu^{++} ions or colloidally dispersed $Cu(OH)_2$ for reduction by sugar or other readily oxidized organic materials. The precipitation of cuprous oxide disturbs the equilibrium: complex copper tartrate $\rightleftharpoons$ reactive Cu^{++} ions. The latter are consumed and then resupplied as long as reducing sugar is available. Accordingly, the frequent assumption that the active constituent of Fehling's solution is the complex copper tartrate is incorrect. The actual reactant is the Cu^{++} ions furnished by the complex ions. This is proven by the fact that Fehling's solution does not appreciably oxidize reducing sugars in the cold, even though it assuredly contains a high concentration of complex copper tartrate. Only when warmed does the latter dissociate sufficiently to furnish enough active non-complex copper ions to accomplish a rapid oxidation of the sugar. Consequently, this reagent serves merely as a reservoir of water-soluble complexly bound copper, which, on

[65] G. P. PAMFIL, *Z. anorg. allgem. Chem.* **133**, 263 (1924); see also G. P. PAMFIL and M. WONESCH, *ibid.* **138**, 199 (1924).

[66] H. FEHLING, *Ann.* **72**, 106 (1849).

demand, delivers reducible, non-complex copper ions or colloidally dispersed $Cu(OH)_2$. Doubtless, other water-soluble, alkali-resistant copper complexes will be discovered, which can be used in place of Fehling's solution.[67] In fact, it is entirely possible that eventually a copper complex will be found which will react with alkaline sugar solutions even in the cold. Such a reagent would present quite an advantage in the detection and determination of sugars. The chemical basis of the Nylander test[68] for sugars, in which black metallic bismuth is precipitated by reduction of an alkaline tartrated bismuth solution, is quite analogous to that of the Fehling test. The complex bismuth tartrate, when warmed, delivers Bi^{+++} ions or colloidally dispersed $Bi(OH)_3$, which then react with the sugar.

A further example of the utilization of a masked system as a reagent is the familiar Nessler solution, so widely employed in the detection and determination of ammonia. This alkaline solution of $K_2[HgI_4]$ produces a yellow precipitate with ammonia. When not more than slight amounts of ammonia are involved, only a yellow color develops, because the precipitate remains colloidally dispersed. This system provides the basis for a convenient colorimetric method of determining ammonia. For many years, the reaction product was supposed to be oxydimercuriamide iodide, or the iodide of Millon's base. It was shown by Nichols and Willits[69] that this assumption is erroneous; the product has the empirical formula $Hg_2I_3NH_2$. The production of this material can be pictured as follows: The traces of HgI_2 provided by the complex equilibrium:

$$[HgI_4]^{--} \rightleftharpoons HgI_2 + 2I^-,$$

react:

$$HgI_2 + NH_3 + KOH \rightarrow KI + H_2O + HgNH_2I.$$
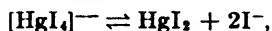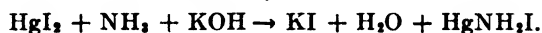
The latter compound (mercuriamido iodide) then combines with HgI_2 to form $HgNH_2I \cdot HgI_2$, i.e., $Hg_2I_3NH_2$.[70]

Another relevant instance is provided by basic lead acetate, which is

[67] C. Neuberg and his collaborators [Exptl. Med. Surg. 1, 399 (1943)] have shown that both aldoses and ketoses cause a precipitation of Cu_2O from a hot solution of $CuSO_4$ masked with $Na_5P_3O_{10}$ (see p. 73). Remarkably, this reduction occurs even if no alkali hydroxide is added.

[68] E. Nylander, Z. anal. Chem. 23, 440 (1884).

[69] M. L. Nichols and C. O. Willits, J. Am. Chem. Soc. 56, 769 (1934).

[70] $HgI_2 \cdot HgNH_2I$ may be represented coordinatively as a binuclear compound

. There is a possibility that the mercury atom is partly held in a cation: $[HgHgI_2NH_2]$.
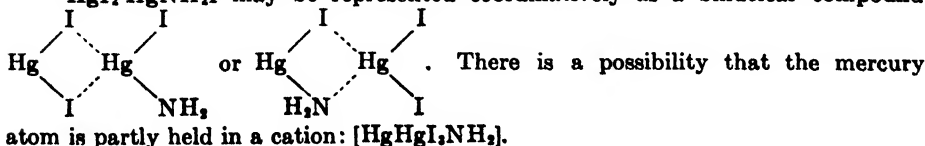
frequently employed as a quasi-soluble lead hydroxide in organic analysis
and preparative organic work for the precipitation of albuminous mate-
rials, dyes, tannins, etc. Basic lead acetate solution is produced as a
strongly alkaline liquid by dissolving lead hydroxide or oxide in water
solutions of normal lead acetate. The solubility of lead hydroxide or
oxide in solutions of lead acetate or alkali acetate is due to the same
causes that are responsible for the selective solubility of lead sulfate in
alkali acetate solutions. In both instances, the lead ion concentration
is decreased so greatly that the precipitation of lead as hydroxide or
sulfate is masked (see p. 89). The application of alkali acetate solutions
of lead sulfate as a reagent for barium is discussed on p. 162.ˈ A survey
of the foregoing examples makes it evident that they are all masked
reaction systems, which become precipitants because they serve as reser-
voirs for active $Cu(OH)_2$, $Bi(OH)_3$, HgI_2, from which these materials are
constantly replenished to the same extent as they are consumed.

Another analytical application of a partially masked reaction system
is possible. The incomplete masking of an ionic species signifies that its
concentration is lowered and kept constantly at the level corresponding
to the dissociation equilibrium of the complex ions. In other words,
the addition of a masking agent can accomplish the same sort of lowering
of an ionic concentration as results from very great dilution of the solu-
tion. Precipitation from extreme dilutions will be discussed in detail
later (see p. 627) but here it will suffice to state that, in general, the
form of a precipitate and its purity are greatly improved by this expedient.
Consequently, an incomplete masking may provide these favorable con-
ditions of low ionic concentration, but without the disadvantage of
enormously increasing the volume of the liquid. This very convenient
device can be particularly useful in gravimetric determinations, where
purity of precipitates and ease of filtration are especially important.

In the great majority of cases, the prevention of color and precipita-
tion reactions, because of the presence of masking agents, can be charged
to the formation of soluble complex compounds as the result of rapid
and practically complete reactions with the masking agent or its ions.
Consequently, it has become customary in many quarters to regard the
masking of reactions as being due invariably to the production of complex
salts.[71] This assumption cannot be justified because masking can be

[71] In recent French publications [compare *Anal. Chim. Acta* 1, 11, 18 (1947)] the
term *complexer* (to form a complex) has been used instead of "masking." Apart from
the fact, as shown in this chapter, that a reaction masking may be due to causes other
than the formation of complex compounds, it should be noted that production of a
complex does not necessarily lead to the prevention of a reaction. The pivotal point
is not merely to produce a complex, but to bring about the formation of such complex
compounds as are capable of preventing the occurrence of certain reactions. The term

brought about by causes other than the production of stoichiometrically defined complex compounds. The masking of metal salts that are in true solution involves the diminution of the concentration of a particular ionic species to a point at which the concentration necessary for the occurrence of a color or precipitation reaction cannot be exceeded. However, this decrease need not result solely from the formation of complex ions. Sometimes the same effect can be secured as a consequence of the production of water-soluble, abnormally dissociating principal valence compounds. Two types of the latter need to be considered. The first type comprises the so-called pseudo-salts (more correctly water-soluble pseudo-salts) which dissociate little or not at all in aqueous solution. The second type includes those principal valence compounds which are produced by a condensation reaction of the masking agent. Mercuric cyanide (see p. 114) is a good example of a pseudo-salt. Because of an inadequate concentration of Hg^{++} and CN^- ions, numerous reactions of these ionic species are not displayed by aqueous solutions of this salt. Consequently, reactions of Hg^{++} ions can be masked by adding alkali cyanides and, conversely, mercuric salts mask the reactions of CN^- ions.

Lead acetate is the classic example of the masking of reactions through the formation of a slightly dissociating principal valence compound. It has long been known that lead sulfate and hydroxide are soluble in excess alkali acetate, and consequently, neither of these compounds can be precipitated from a lead solution that also contains much alkali acetate. Several workers[72] have found that the reason is not the formation of complex lead acetates but the production of normal lead acetate, whose innately low ionic dissociation is decreased still more by the mass action effect of the excess alkali acetate. Consequently, the end-effect of lowering the Pb^{++} ion concentration is accomplished by alkali acetate in a manner that is quite analogous to that of a masking agent which operates by producing complex salts or ions.

Other examples of reaction maskings that are probably chargeable to the presence of pseudo-salts can be cited. For instance, Scheibler[73] observed that no barium sulfate settles out, even after long standing, when sulfuric acid is added to a solution of the barium salt of arabinic acid. The calcium salt of pyrocatecholdisulfonic acid on treatment with excess alkali carbonate in the cold gives only an incomplete precipitation

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complex formation, therefore, does not suffice to give an exact representation of the meaning of a reaction masking.

[72] Compare A. A. Noyes and W. H. Withcomb, *J. Am. Chem. Soc.* **27**, 747 (1905); T. T. Fox, *J. Chem. Soc.* **95**, 857 (1909); S. M. Edmonds and E. Birnbaum, *J. Am. Chem. Soc.* **62**, 2367 (1940).

[73] C. Scheibler, cited in *J. Chem. Soc.* **30**, 538 (1876).

of calcium carbonate, even after several hours standing, whereas reaction occurs promptly on warming.[74]   In this salt, the calcium replaces only the hydrogens of the sulfonic groups. Complex formation is hardly likely, and it is logical to suppose that this is a pseudo-salt.   In warm aqueous solutions, it presumably furnishes enough Ca^{++} ion to exceed the solubility product of calcium carbonate, but in the cold the dissociation is inadequate.   In line with this reasoning is the fact that calcium phosphate and oxalate, whose solubility products are less than that of calcium carbonate, are precipitable even from cold solutions of calcium pyrocatecholdisulfonate.

Bergmann and Bondi[75] found that the precipitation of silver as chloride from dilute nitric acid solution can be prevented by styryl-β-phosphinic acid, $C_6H_5 \cdot CH \!=\! CH \cdot PO_3H_2$, or similar unsaturated phosphinic acids of the general type $R_1R_2C \!=\! CH \cdot PO_3H_2$.   In these cases also, the formation of soluble non-dissociating silver salts is much more probable than the production of complex silver ions, especially if it is remembered that, with the exception of $H[AgCl_2]$, no acid-stable soluble silver complex salts have been discovered as yet.   It is remarkable that the masking action of styryl-β-phosphinic acid is nullified by halogen substitution. For instance, the chloro-substituted acid $C_2H_5C(Cl) \!=\! CH \cdot PO_3H_2$ is without effect on the precipitation of silver chloride.[76]

It is quite possible that the interesting preventions of precipitation by alkali salts of cellulose sulfuric acid esters, observed by Traube and his coworkers, and ascribed to protective colloid action (see p. 481) are related to the formation of pseudo-salts of these polyatomic ester acids.[77a]

In addition to pseudo-salts, there is, as noted on p. 89, a second type of principal valence compound, production of which can be the reason for the masking of a reaction.   These are stable, soluble products of condensation reactions of the masking agent with molecules or ions of the compound to be masked.   Relevant instances are the facts (see p. 77) that hydrogen peroxide can mask numerous reactions of molybdic or tungstic acids or their respective anions.   Permolybdic and pertungstic

[74] F. FEIGL and H. G. DE CARVALHO, Unpublished studies.

[75] E. BERGMANN and A. BONDI, Ber. 63, 1167 (1930).

[76] E. BERGMANN and A. BONDI, Ber. 66, 281 (1933).

[77a] Along this same line is the interesting observation by M. V. RINE [Z. anal. Chem. 37 (1898)] that strontium pyrophosphate, in contrast to $Ba_2P_2O_7$, is quantitatively dissolved by warming with dinitro-p-benzoylbenzoic acid.   Since this acid is extremely weak, and can hardly function as a complex-former, and since Sr^{++} ions are known to show but very slight tendency to enter into complex ions, it seems logical to assume that $Sr_2P_2O_7$ dissolves in this nitro acid by forming a pseudo-salt.   If this is true, the precipitation of strontium by alkali pyrophosphate should be prevented by the presence of dinitro-p-benzoylbenzoic acid.   The experiment has not been tried, nor has there been any report of the position of the nitro groups in this acid.

acids (H_2MoO_5 or H_2WO_5), *i.e.*, principal valence compounds, are produced by condensation of molybdic or tungstic acid and hydrogen peroxide.[77b]

Interesting instances of masking that are due to the production of principal valence compounds are provided by the action of fluoride ions in molybdate and tungstate solutions. All precipitation and color reactions of these substances, and likewise many reactions of vanadate ions, are prevented.[77c] Stable fluorinated metal acids, or their ions, are formed immediately in aqueous solutions, and when excess fluoride ions are present the reactions are practically quantitative. This masking of MoO_4^{--}, WO_4^{--}, and VO_3^- ions can be represented by the following typical equation:

$$MoO_4^{--} + 4HF \rightleftharpoons (MoO_2F_4)^{--} + 2H_2O$$
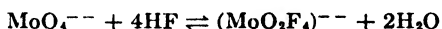
Among other instances of maskings because of the formation of principal valence compounds are the familiar failures of metals of the ammonium sulfide group to respond to carbonate and hydroxide precipitants in the presence of glycerol, sugars, and other aliphatic polyhydroxy compounds. Traube and his collaborators[78] elucidated these reaction maskings. They succeeded in isolating the light yellow crystalline barium salt (likewise the Ca and Sr salts) from the alkaline, yellow, iron-bearing solutions masked with mannitol. By reaction with sodium sulfate, the barium salt (I) yielded the crystalline sodium salt (II). A barium-iron salt (III) was isolated from an iron solution masked against hydroxide precipitation by gluconic acid, which is a polyhydroxycarboxylic acid closely related to mannitol.
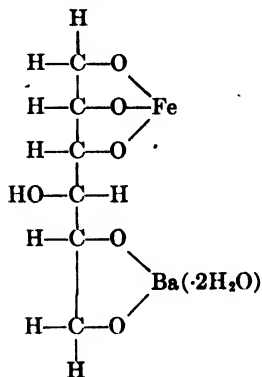
(I)
Slightly soluble in water
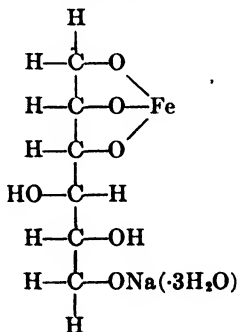
(II)
Quite soluble in water
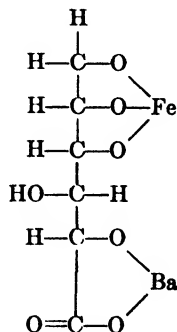
(III)
Slightly soluble
in water

[77b] F. FEIGL and I. D. RAACKE, *Anal. Chim. Acta* **1**, 317 (1947).

[77c] F. FEIGL, *Anal. Chim. Acta* **2**, 312 (1948).

[78] W. TRAUBE and F. KUHBIER, *Ber.* **65**, 187 (1932); W. TRAUBE and H. HARTING, *Ber.* **66**, 1545 (1933).

Analogously constructed ferric compounds, with the ratio Ba(Ca, Sr):
Fe:polyhydric alcohol = 1:1:1, as well as the corresponding mono-
alkali salts were obtained from arabitol, sorbitol, glucose, D-mannose,
maltose, and levulose, i.e., from carbohydrates with at least five adjacent
OH groups. The Al-Ba, Cr-Ba, and Co-Ba-mannitol salts, completely
analogous to the foregoing Fe-Ba salts, were isolated. Glycerol solutions
yielded a Ba-Fe-glycerinate, $Ba_2Fe(OH)(C_6H_{10}O_6)$. Thus, there is no
doubt that the failure of alkali hydroxide to precipitate the metals of the
ammonium sulfide group is due to the fact that the metals form principal
valence compounds with sugars, etc., by condensation of the metal
hydroxides with polyhydric alcohols.[79]

This action of polyhydric alcohols is not limited to tri- and quadriva-
lent metal ions. The precipitation as hydroxides of certain divalent
metals is similarly masked. The prevention of the precipitation of
$Cu(OH)_2$ seems to be due to the production of compounds which, in
composition and structure, exhibit an analogy to the iron compounds of
polyhydric alcohols. For instance, a water-soluble Na-Cu-glycerinate
has been isolated.[80] This compound can be represented by (I) in which
the copper is bound anionically. The replacement of hydrogen atoms of
alcoholic OH groups by copper plays a part in the prevention by poly-
hydroxy-carboxylic acids of the precipitation of $Cu(OH)_2$. Tartaric
acid is especially important in this respect, because this acid or its alkali
salts are used in preparing alkaline Fehling's solution, so widely used in
the detection and determination of reducing sugars. The question as to
which copper compound is contained in Fehling's solution is often dis-
missed with the bare declaration that copper complexes are present, but
without any details as to their constitution. Sometimes the active
compound is said to be a sodium-copper tartrate as represented by (II).

[79] This assumption is strengthened by the finding that solutions masked by poly-
hydric alcohols are obtained best by treating the metal solution with the masking
agent and then adding alkali hydroxide, or by adding an alkaline solution of the
particular polyhydric alcohol to the metal salt solution. Precipitates of metal
hydroxides are often only partially dissolved by alkaline solutions of polyhydric
alcohols; sometimes colloidal solutions result. Obviously, the activity of metal
hydroxides in statu nascendi is a factor (see Chapter VI, remarks on pyrocatechol).
The following observations are in harmony with the foregoing remarks. The addition
of Na_3PO_4 produces no precipitate of $FePO_4$ if the iron-mannitol complex has been
formed in an alkaline solution. On the other hand, a ferric solution that has been
treated with mannitol is not masked against precipitation by Na_3PO_4. Accordingly,
masking by polyhydric alcohols clearly is dependent on the possibility being provided
for the condensation, in an alkaline medium, between the alcohol and ferric hydroxide
(best in the nascent condition). In the case of mannitol, the formation of compound
(II) is involved.

[80] F. Bullnheimer, Ber. 31, 1453 (1898).

Since both of these statements are inadequate, it is apropos to include here several critical remarks that are based on the fundamental studies by Bullnheimer.[81] It is an established fact that one mole of tartaric acid prevents the precipitation of one mole of $Cu(OH)_2$ if an excess of alkali is present. The compound (II) has been actually isolated; it contains two atoms of alkali metal and one atom of copper for each molecule of tartaric acid.
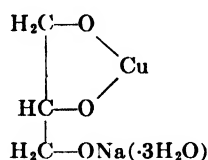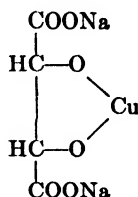
(I)   (II)

Patently, (II) is not a complex compound, but a principal valence compound which, with respect to the binding of the copper, corresponds to sodium-copper glycerinate (I). Bullnheimer objected to accepting (II) as the active component of Fehling's solution. He pointed out that, although an aqueous solution of this salt is stable at room temperatures, it decomposes when heated and deposits $Cu(OH)_2$. In contrast, Fehling's solution is not decomposed by boiling; in fact it must be used hot for the oxidation of reducing sugars. This objection, which at first sight seems to be valid, is not really justified. It should not be overlooked, that a precipitation of copper hydroxide from a solution of (II) is based on the reversible hydrolysis:
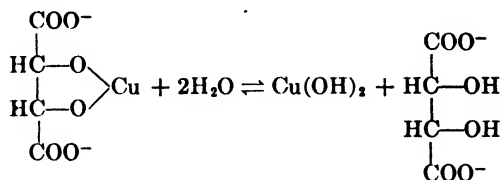
However, Fehling's solution always contains an excess of tartrate and thus, through mass action effect, sets up the possibility of preventing the hydrolytic precipitation of $Cu(OH)_2$. Consequently, the assumptions that Fehling's solution contains (II) and that a masking is due to the formation of this compound seem entirely admissible, at first. A more forceful objection to the activity of (II) in Fehling's solution is the fact that Bullnheimer succeeded in isolating the heat-stable compound (III) from a copper solution masked with Rochelle salt. Considered from the purely formal standpoint, (III) consists of the components (*a*) and (*b*).

[81] F. Bullnheimer and E. Seitz, *Ber.* **32**, 2347 (1899); **33**, 817 (1900).

The postulate that this is a double salt is controverted by the fact that double salts in general decompose into components that are capable of independent existence. However, a component as shown in (b) does not exist, because only bi-alkali and not tetra-alkali salts of tartaric acid are known. If, however, the Bullnheimer compound is regarded as an inner complex compound as shown in (IV), then the large number of alkali atoms becomes entirely intelligible.

(III)   (IV)
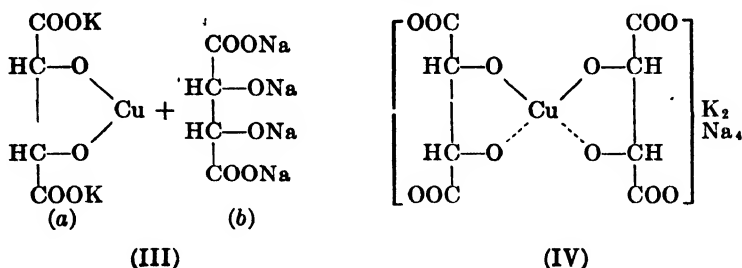
Accordingly, the question whether the masking of copper in Fehling's solution is due to the production of a principal valence compound (II), or of a complex compound (IV), cannot be definitely decided at present, since sound arguments can be advanced in favor of both of these types of compounds. It must also be noted that the isolation of a compound of definite composition from a solution is a strong indication, but by no means is an absolutely certain proof, that only this compound is also contained in the solution. Hence, it is entirely possible that both (II) and (IV) are present in varying amounts in Fehling's solution and are active there. In any event, (II) demonstrates that a masking may also result from the production of an abnormally dissociating principal valence compound, so that this explanation was adopted also for the masking of the hydroxide precipitation of tri- and quadrivalent metals in the presence of polyhydroxy compounds. Consequently, there is every reason to expect that new masking agents will be discovered also among compounds that are not typical complex formers.

Potassium periodate is an inorganic masking agent which prevents the hydroxide precipitation of metals. It functions by forming water-soluble principal valence compounds. The addition of excess potassium periodate to solutions of many non-oxidizable metal salts results in precipitates which dissolve when potassium hydroxide is introduced. For example, even at the ratio 1 Fe^{III}:1 KIO_4, the iron comes down quantitatively as a yellow precipitate which, on the addition of potassium hydroxide, gives a brown solution.[82] The precipitation and subsequent solution can be represented:

[82] F. FEIGL and L. I. MIRANDA, unpublished studies.

$$Fe^{+++} + IO_4^- + H_2O \rightarrow Fe\underset{\diagdown O}{\overset{\diagup O}{-}}O\underset{\diagdown O}{\overset{\diagup O}{-}}I + 2H^+ \ldots (1)$$

$$Fe\underset{\diagdown O}{\overset{\diagup O}{-}}O\underset{\diagdown O}{\overset{\diagup O}{-}}I + 2K^+ + 2OH^- \rightarrow Fe\underset{\diagdown O^-}{\overset{\diagup O}{-}}O\underset{\diagdown O^-}{\overset{\diagup O^-}{-}}I{=}O + 2K^+ + H_2O \ldots (2)$$
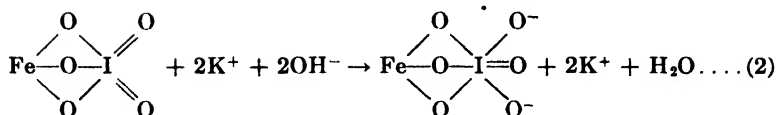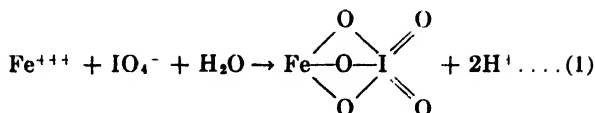
The ferric compound, precipitated as shown in (1), is a salt of the hypothetical *meso*-periodic acid $H_3IO_5 = IO_2(OH)_3$. The latter may be regarded as the monohydrate of metaperiodic acid HIO_4.[33] This tribasic acid is not stable, but its lead and silver salts have been isolated. Likewise, the dihydrate of metaperiodic acid, $HIO_4 \cdot 2H_2O = H_5IO_6 = IO(OH)_5$, is known. It is called *para*-periodic acid and is present in the product of (2). Here the ferric atom salifies three of the five hydroxyl groups of the acid and produces a divalent anion and two K^+ ions. The iron in this principal valence compound is masked against precipitation by OH^-, CO_3^{--}, or PO_4^{---} ions, and even against 8-hydroxyquinoline. The tendency to form the iron-bearing anion is so marked that $Fe(OH)_3$ precipitated from ferric solutions by excess potassium hydroxide goes into solution on the addition of potassium periodate. Other trivalent, and also di- and quadrivalent, metal ions show a similar behavior toward potassium periodate and hydroxide, and a mechanism analogous to that just given probably applies in all such cases. The author and his associate noted the interesting divergent behavior of lanthanum. The addition of potassium periodate to a solution of lanthanum salts produces a precipitate which does not dissolve in potassium hydroxide. In contrast, the salts of yttrium, scandium, and erbium behave similarly to those of iron and other trivalent metals. Possibly, analytical use can be made of this exceptional behavior of lanthanum.

Interest in the behavior of ferric ions toward potassium periodate and hydroxide goes beyond the fact that it provides an instance of masking due to the formation of a water-soluble principal valence compound. Pročke and Uzel[34] showed that an alkaline ferric periodate solution is a very sensitive and selective precipitant for lithium ions. Obviously, $LiK[FeIO_6]$ is produced. If certain reaction conditions are maintained, it is also possible to detect lithium in the presence of sodium, even though the latter likewise forms a difficultly soluble $Na_2[FeIO_6]$. The production of slightly soluble sodium salts is the reason for using potassium and not

[33] See J. W. MELLOR, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. II, p. 386 ff., New York, 1937, concerning the nomenclature of the hydrates of I_2O_7.

[34] O. PROČKE and R. UZEL, *Mikrochim. Acta* **3**, 105 (1938).

sodium hydroxide when dissolving metal *meso*-periodates. It is striking that only Li^+ and Na^+ ions are capable of precipitating $[FeIO_6]^{--}$ ions. In contrast, the ions of the alkali metals of higher atomic weight or of greater atomic radius (K^+, Rb^+, Ca^{++}, NH_4^+) are inactive. An additional point of interest is that copper is stabilized in the trivalent state in the soluble, yellow-red alkali-copper[III]-*meso*-periodates. Feigl and Uzel[86] used this fact as the basis of sensitive tests for periodic (*meta*) acid. The foregoing examples demonstrate that a further reason for studying the chemism of reaction maskings is that masked reaction systems sometimes may also serve as selective reagents (see pp. 86–88).

A principal valence masking by an organic compound, through which ... ... is prevented from exhibiting familiar reactions. is found in the ... ... + formaldehyde. For aldehyde-sulfite ... ...

$$CH_2O + SO_3^{--} + H_2O \rightarrow H_2C\!\!<^{OH}_{SO_3^-} + OH^- \quad \text{or} \quad CH_2O + HSO_3 \rightarrow H_2C\!\!<^{OH}_{SO_3^-}$$
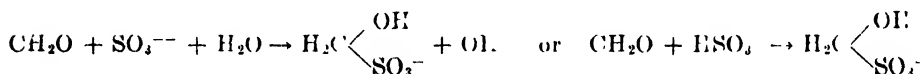
The concentration of free SO_3^{--} ions is so low in solutions of these salts, that no oxidation by iodine to sulfate, nor precipitation of barium sulfite by barium chloride, occurs. Both of these effects can be put to analytical use (see p. 341).

It may also be expected that occasionally typical complex-formers can depart from their usual action and also bring about maskings through principal valence binding of a metal atom. An instance of this atypical behavior is found in the action of tartaric acid toward Sb^{+++} ions. It is well known that the precipitation of antimony by potassium hydroxide does not occur if tartaric acid or a tartrate is present. Instead, a soluble potassium-antimony salt of tartaric acid (tartar emetic) is produced. This is usually assumed to be potassium antimonyl tartrate as shown in (I). In view of the fact that antimonyl chloride, SbOCl, is insoluble in water, it seems improbable that a cationically bound SbO group would be resistant to ammonia or alkalies. Consequently, the isomeric structure (II) seems more likely. In this, the antimony is a constituent of an anion and linked through principal valences to the carboxyl group and two adjacent alcoholic OH groups:

$$
\begin{array}{cc}
\begin{array}{l}
\text{COO(SbO)} \\
| \\
\text{HC—OH} \\
| \\
\text{HC—OH} \\
| \\
\text{COOK}
\end{array}
&
\left[
\begin{array}{l}
\text{COO} \\
\quad\quad\diagdown \\
\text{HC—O—Sb...OH}_2 \\
\quad\quad\diagup \\
\text{HC—O} \\
| \\
\text{COO}
\end{array}
\right] \text{K}
\\
\text{(I)} & \text{(II)}
\end{array}
$$
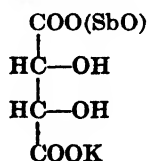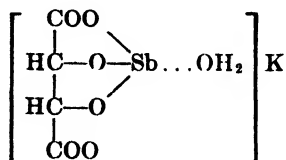
[86] F. Feigl and R. Uzel, *Mikrochemie* **19**, 133 (1936).

It is entirely possible that the masking of the precipitation of bismuth hydroxide in the presence of tartrates is due to the formation of an analogous compound.

An interesting example of a reaction masking that probably is due to the formation of a water-soluble principal valence compound from a water-soluble complex compound is found in the behavior of the aqueous system: ferric iron + "ferron" (7-iodo-8-hydroxyquinoline-5-sulfonic acid). This reagent (I) reacts selectively (see p. 187) in acid solution, with ferric salts to form a blue, water-soluble compound, in which the iron is a constituent of an inner complex anion (II). If the blue solution is made basic with an alkali hydroxide, ferric hydroxide precipitates. On the other hand, alkalizing with ammonia or alkali carbonate produces no precipitate, but, instead, the blue solution turns brownish yellow. Accordingly, there is masking toward the OH⁻ ion in concentrations furnished by these basic materials. Experiments by the writer and his associate, C. Soria, have shown that ammonia or soda produces no precipitate, even after prolonged heating, if the ratio of iron to ferron is 1:1. This finding indicates that the masking cannot be due to the formation of an alkali salt of (II), because this would demand the ratio 1:3. In addition, there is no reason to expect that salt production at the SO_3H group would cause the color to change from green to brown-yellow. Consequently, it is likely that a basic principal valence compound with the formula (III) is formed and it produces so little Fe^{+++} ion in water solution that the solubility product of $Fe(OH)_3$ is not exceeded on the addition of ammonia or alkali carbonate. Correspondingly, an ammoniacal solution of ferron dissolves freshly precipitated hydrous ferric oxide, that has been thrown down by ammonia or sodium carbonate.

$$\text{(I)} \qquad \text{(II)} \qquad \text{(III)}$$
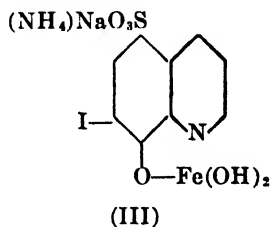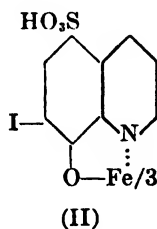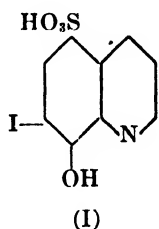
Compound (III) could not be isolated. It may also be formed from solutions of (II), i.e., in the presence of excess ferron. In this case one mole of (II) is converted into one mole of (III), with formation of two moles of the alkali salt of (I). The addition of hexamminocobaltic chloride (luteo chloride) to an ammoniacal solution of (III) produces a brown precipitate, which might be a luteo salt of (III). There seem to be

analogously constructed aluminum, bismuth, zirconium, and thorium compounds of ferron, since no precipitate forms when ammonia or alkali carbonate is added to the respective acidified salt solutions in which the ratio of Al(Bi, Zr, Th) to ferron is 1:1. In these cases also, as with iron, a precipitate can be obtained by adding luteocobaltic chloride to the ammoniacal solution.

Masking, in the general sense, is the prevention of reactions whose occurrence is normally to be expected. Accordingly, the common limitation of the term "masking" to the production of abnormally reacting complex compounds has not been accepted here, but the formation of abnormally dissociating principal valence compounds has also been included as a cause of reaction masking. However, another step must be taken along this road. Examples of masking can be cited which are ascribable to still other factors than the production of stoichiometrically defined complex or principal valence compounds. For instance, materials may be adsorbed from solutions and their normal reactivity may be more or less decreased when they are thus resident on the surface of another material. In such cases, the adsorbent functions as a masking agent and the practical effect may be entirely comparable with the action of soluble masking agents. Several pertinent demonstrations can be conducted on filter paper (S. & S. 601) with comparison drop reactions carried out on a spot plate.[86] For example, a solution of methylene blue is rapidly reduced by alkali sulfide to produce the colorless leuco compound of the dye. If a drop of the dye solution is placed on a disk of filter paper and the latter then placed in the depression of a spot plate and covered with two drops of sodium sulfide solution, the discharge of the color is much slower than when a drop of the methylene blue solution is treated directly on a spot plate with two drops of sodium sulfide solution, i.e., in the absence of the paper. The formation of black copper oxide from blue cupric hydroxide provides another example. This dehydration proceeds very rapidly in a microcrucible, if a mixture of one drop of dilute copper solution and one drop of sodium hydroxide is warmed. In contrast, when a drop of the copper solution is spotted on filter paper with a drop of the alkali, no blackening occurs even when the paper is warmed to 110°C. Another striking instance is provided by a comparison of the reaction of gold salts with p-fuchsine (see p. 311) on paper and on a spot plate. No reaction can be seen if a drop of the gold solution is allowed to soak completely into the paper and then treated with a drop of the dye solution. A blue-brown precipitate, due to a gold fuchsine compound, forms immediately on a spot plate. The difference can be accounted for by assuming that gold ions are adsorbed on the

[86] F. FEIGL and P. W. WEST, unpublished studies.

paper and when held in this fashion they react only slowly with fuchsine. This postulate is strengthened by the observation that the precipitate forms quickly, even as a spot reaction on paper, if the fuchsine is put on the paper first and treated there with the·gold solution. Under these conditions, there is no time for the adsorption of the gold. Paper acts as a masking agent in these instances. These experiments further demonstrate that, as a consequence of adsorption, the sensitivity of spot reactions can be affected by the order in which drops of the test solution and reagent are brought onto the paper.

Adsorption is also responsible for the reaction maskings that are sometimes observed in colloidal solutions, which of course contain surface-rich systems. Protected hydrosols (see Chapter X) are especially worth considering in this connection, because not only the visibility of reaction products may be less under such circumstances, but even their reactivity may be lower. Pseudo-solutions exhibit masking effects far less often, and the maskings are always less permanent than those encountered in true solutions. This is to be expected because colloid systems in general are not stable. Instances of colloidal masking will be given in Chapter X.

The discussion of the reaction masking of dissolved materials should also include some points relative to the behavior of organic compounds. Instances have been given which show that organic·compounds can likewise lose their normal reactivity through incorporation in soluble principal valence and complex compounds. Pertinent examples are (a) the masking of CN^- ions by the addition of Hg^{++} ions to produce soluble, non-dissociating $Hg(CN)_2$; (b) the masking of oxalic acid by its incorporation in complex molybdenooxalic acid. Among the further instances that·can be cited are. the following: (c) the reactions of aldehydes and ketones are masked by the addition of alkali sulfites and bisulfites because of the formation of aldehyde and ketone bisulfite compounds; (d) the water-insoluble organic bases α,α'-dipyridyl and α,α'-phenanthroline form such stable unions with Fe^{++} ions in acid solution that the bases are not precipitated at room temperature if alkali hydroxide is added to the resulting hexammine anions (see p. 319); (e) palladium dimethylglyoxime dissolves in potassium hydroxide solution (see p. 276) and the subsequent addition of an ammoniacal nickel solution produces no red precipitate, and so the dimethylglyoxime is masked in the soluble alkali-palladium-dimethylglyoxime compound. (f) Pyrocatechol rapidly reduces ammoniacal silver salt solutions to the metal. However, this reducing action is lost if the reagent is present as the ammonium salt of bismuth-pyrocatechinic acid, where it is complexly bound (see p. 361).

One factor is common to all the foregoing examples of the masking

of organic compounds. In every case an inorganic compound acts as the masking agent, and does so by combining with the particular organic material to form a stable principal valence or complex compound. Up to the present, no attention seems to have been given to utilizing the masking of the reactions of organic compounds in the field of organic analysis. This is partly because there are relatively few water-soluble purely organic compounds.

There is still another type of masking the reactivity of organic compounds that is *not* based on the production of principal or auxiliary valence compounds. Quite often, one and the same group, which reacts in characteristic fashion in certain organic compounds, completely loses this reactivity when it forms a part of other organic compounds. In such cases, the loss of reactivity is due to other groups that are likewise present in the molecule, but which do not appear as active participants in the equation depicting a reaction. Such interference with the reactivity of a group because of the effect of other groups of the same molecule is encountered only among organic compounds. It can be regarded as an inter- or intramolecular irreversible masking. This type of reaction masking has great significance in qualitative organic analysis, because it may impair the specificity and selectivity of tests for certain organic groups. The fact that other groups in the molecule can exert an influence is important also in studies of the relation between the activity of organic reagents and certain groups contained in them. Relevant instances are discussed in Chapters VI–IX.

The preceding discussion has dealt exclusively with the masking of reactions in systems of dissolved materials. The question may fairly be asked whether water-insoluble materials are also susceptible to a reaction masking that is comparable with the effects encountered among solutions. The answer is in the affirmative, at least with respect to the reactions of insoluble inorganic compounds. Numerous cases are known in which a solid loses its normal reactivity toward certain reagents because it is associated with a second solid, which thus plays the part of a masking agent. Experience has shown repeatedly that the coprecipitation of two ionic species by the same reagent may produce precipitates whose behavior toward appropriate reagents is quite different from that of a mere mixture. Sulfide precipitates offer a veritable treasure trove of such abnormalities. For example, MnS coprecipitated from alkaline solutions with ZnS, CdS or HgS is quite resistant to acetic acid, although this acid readily dissolves manganous sulfide when the latter is unaccompanied. In fact, MnS coprecipitated with HgS is not readily attacked by even mineral acids. On the other hand, HgS that has been

brought down along with MnS or CdS loses much of its solubility in sodium sulfide, *etc.*[87]

Excellent examples of the masking of the components of coprecipitated mixtures are found among slightly soluble sulfates. Calcium sulfate is soluble in concentrated solutions of sodium thiosulfate, probably because of the production of the complex $Na_2[Ca(S_2O_3)_2]$. Diehl[88] reports that it can thus be completely extracted from a mixture of separately prepared $CaSO_4$ and $BaSO_4$. However, when these sulfates are coprecipitated, it is not possible to separate them by means of thiosulfate, because, as observed by Fresenius,[89] much of the $CaSO_4$ does not go into solution. Lead sulfate is easily soluble in alkali acetate solutions (see p. 89), whereas barium sulfate is practically insoluble in these solutions. This selective solubility is often applied in analytical procedures to separate $PbSO_4$ from SiO_2, *etc.* Majdel[90] showed that an ammonium acetate solution of sufficient strength to smoothly dissolve $PbSO_4$ that had been precipitated alone, is not capable of removing all of the lead sulfate from a $BaSO_4$-$PbSO_4$ mixture produced by coprecipitation. He found that the interference begins to appear at the ratio Ba:Pb = 1:10, and increases with rising proportions of barium until the $PbSO_4$ becomes practically insoluble in a particular ammonium acetate solution. Scott and Alldredge[91] believe that the rate of solution is decreased rather than that there is an impairment of the actual solubility of $PbSO_4$ in ammonium acetate, since prolonged and repeated (8-12 times) digestion with this solvent eventually brings about complete solution of the $PbSO_4$.

For practical analytical purposes, both a partial impairment as well as the complete prevention of the reactivity of the constituents of coprecipitated products are of importance, since in either case deviations from the normal expected behavior appear. The fact that the behavior of coprecipitated materials often differs markedly from the normal behavior of mechanically prepared mixtures of the components, has a great bearing on reaction specificity. Consequently, this topic will be treated in further detail in Chapter V, where induced reactions are discussed. As to the chemical basis of the masking of the reactivity of the components of coprecipitates, it is assumed here that the production of complex

[87] F. FEIGL, *Z. anal. Chem.* **65**, 25 (1924); *Z. anorg. allgem. Chem.* **157**, 251, 269 (1926).

[88] C. DIEHL, *J. prakt. Chem.* **79**, 430 (1860).

[89] R. FRESENIUS, *Z. anal. Chem.* **30**, 458 (1891).

[90] J. MAJDEL, *Z. anal. Chem.* **83**, 36 (1931).

[91] W. W. SCOTT and S. M. ALLDREDGE, *Ind. Eng. Chem., Anal. Ed.* **2**, 32 (1930).

compounds or of mixed crystals as well as adsorption may play a role. Examples can be cited to demonstrate that one of the components can lose its normal reactivity when incorporated in insoluble complex compounds of stoichiometrically defined composition and composed of two constituents that are capable of independent existence. Feigl[92] found that the sensitive reaction of soluble and insoluble magnesium salts with diphenylcarbazide (development of a red-violet color lake) fails with dolomite, which is the double carbonate $MgCO_3 \cdot CaCO_3$, whereas prompt reaction is secured with magnesite ($MgCO_3$) and mixtures of magnesium and calcium carbonate, with the coprecipitated carbonates, and likewise with ignited dolomite. These differences arise because dolomite is a complex compound, that can be formulated as the calcium salt of a magnesium carbonate complex: $Ca[Mg(CO_3)_2]$. The magnesium carbonate is a stable anionic constituent in this complex compound and thus is masked against diphenylcarbazide. Ignition destroys the complex binding, and the resulting mixture of CaO and MgO again responds normally to the diphenylcarbazide test for magnesium. A convenient and reliable method of differentiating magnesite and dolomite was developed[92] on the foregoing observations.

A further instance of reaction masking in solid complex compounds was found in the behavior of the stable, insoluble salts of hydronickelocyanic acid, which itself is not stable.[93] Such salts are easy to prepare, as they precipitate when metal salt solutions undergo double decomposition with solutions of $K_2[Ni(CN)_4]$. The nickel in suspensions of $Cu[Ni(CN)_4]$, $Zn[Ni(CN)_4]$, etc., is not revealed directly by dimethylglyoxime or other organic reagents. This is readily explained because the nickel is present not as a cation but as part of the anion of the insoluble double cyanide. Solid nickel cyanide, as well as its ammoniacal solution, reacts immediately, but only one-half of the total nickel is converted to the Ni dimethylglyoxime compound. The reason is that nickel cyanide actually is a complex compound and, as shown by the formula $Ni[Ni(CN)_4]$, it is really the nickel salt of hydronickelocyanic acid. Accordingly, its ammoniacal solution contains the ions of the compound $[Ni(NH_3)_2][Ni(CN)_4]$. In either the solid or the ammoniacal solution, only one-half of the nickel is cationically bound and, hence, susceptible to precipitation by dimethylglyoxime.

The foregoing examples demonstrate clearly that masked reaction systems are not confined to dissolved materials, but are likewise possible with solids. Sometimes, this fact must be taken into account when

[92] F. FEIGL, Z. anal. Chem. **72**, 113 (1927); **74**, 399 (1928); see also F. FEIGL and H. LEITMEIER, Centr. Mineral. Geol. **1928A**, 74; Chem. Abstracts **22**, 2903 (1928).
[93] F. FEIGL, V. DEMANT and E. DE OLIVEIRA, Anais. assoc. quim. Brasil **3**, 72 (1944).

making tests. In the final analysis, it makes no difference whether such masking is due to the decrease of the direct reactivity of the solid phase or to its diminished solubility. The important point here is that complex binding, adsorption, or the production of mixed crystals is or may be the basis of a reaction-masking of solid materials. This can show itself both in the lessened reactivity of a solid, as well as in its lowered solubility.

To sum up, the phenomena of reaction masking may not be ascribed exclusively to the production and activity of soluble, stoichiometrically defined, isolable complex compounds. As has been shown, the following additional factors must be considered: (a) the formation of water-soluble principal valence compounds; (b) the selective adsorption of dissolved materials on solid adsorbents; (c) the union of insoluble compounds that are stable when by themselves. This latter factor plays a part in the anomalous behavior of the products formed by coprecipitation. Among organic compounds there is still another factor, namely, the masking of the salt-forming action of certain groups by other groups contained in the same molecule. Consequently, it is easy to see why cases may be encountered in which it is not possible to draw a sharp distinction between the various types of reaction masking. Such differentiation and exhaustive consideration of the details of the chemical basis of a reaction masking may be irrelevant with regard to the use of the effect in analytical practice. If, however, an attempt is being made to derive certain rules from experimental findings, and to discover guiding principles that can be utilized in the search for new masking agents, then it is essential to make an effort to ferret out the reason(s) for the masking effect. If this is done, interesting points of contact with problems considered in other chapters of this book frequently come to light.[94]

[94] An excellent example is the masking of the precipitation of hydrous ferric oxide by polyhydric alcohols (see p. 91). It was found that a certain number and spatial arrangement of OH groups is necessary to the incorporation of an iron atom in the anionic part of the compounds discussed in this chapter. This finding indicates the significance of the presence of certain atomic groupings in organic compounds with respect to salt-formation and the production of selective actions. Further material along this line will be given in Chapter VI. Among the compounds of polyhydric alcohols with iron, which are formed only in alkaline media, special interest attaches to the alkali and alkaline earth salts. In the former, only one OH group is salified by alkali metal, whereas the hydrogens of two adjacent OH groups are salt-forming in the alkaline earth compounds. This shows the importance of ring closures for the stability of salts. The alkali-iron as well as the alkaline earth-iron compounds demonstrate that polyhydric alcohols acquire acidic characteristics only because of the incorporation of the iron. It will be shown in Chapter VI that acidification and strengthening of salt-forming capabilities of organic compounds by their incorporation in complex compounds is by no means rare. Finally, the alkali-iron polyhydric

DEMASKING

If reaction masking, due to the production of a complex, is considered from the standpoint of a chemical equilibrium, the general schematic representation covering such cases shows that the forward process (masking) is not the only possibility. The reverse is also possible, *i.e.*, an ionic or molecular species which is bound in a complex may be freed by removal of the masking agent. The inverse of the masking process is logically termed "demasking." These two processes are pictured in the scheme:

$$A + Ms \rightleftharpoons AMs \qquad \left\{ \begin{array}{l} \text{Masking} \quad = \longrightarrow \\ \text{Demasking} = \longleftarrow \end{array} \right.$$
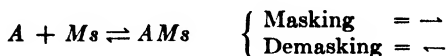
In this expression, A = a molecular or ionic species, Ms = the masking agent, and AMs = the masked molecular or ionic species produced through complex binding.

There are two kinds of demasking which can be clearly distinguished from each other. The first type has been known for a long time and has been used frequently. It consists of the disintegration of complex compounds by radically changing the pH of the aqueous solution. A familiar instance is the decomposition of an ammoniacal silver chloride solution by acids. The $[Ag(NH_3)_2]^+$ ions, which were masked against precipitation by Cl^- ions, are broken down, with formation of NH_4^+ ions, and the Ag^+ ions are set free. They can then be precipitated as AgCl by the Cl^- ions present. All silver salts which are soluble in ammonia or other ammine-forming bases can be demasked in a manner analogous to the one just described. An analytical application of this demasking of silver ammine ions is discussed on p. 86. Many instances of demasking by change of pH are encountered among alkali salts with complex acido anions. Thus the complex cyanide ions $[Ag(CN)_2]^-$, $[Cu_2(CN)_4]^{--}$, and $[Pd(CN)_4]^{--}$ are decomposed by mineral acids, with production of volatile prussic acid and precipitation of acid-resistant AgCN, $Cu_2(CN)_2$, and $Pd(CN)_2$, respectively. Anions of other acid-decomposable complex metal cyanides, such as $[Zn(CN)_4]^{--}$, $[Cd(CN)_4]^{--}$, or $[Ni(CN)_4]^{--}$ are demasked by acids to yield Zn^{++}, Cd^{++}, or Ni^{++} ions, respectively. The decomposition of $[Co(NO_2)_6]^{---}$, $[Ag(S_2O_3)_2]^{--}$, and $[Cu(CO_3)_2]^{--}$ ions by mineral acids, to yield Co^{+++}, Ag^+, and Cu^{++} ions, belongs in this category. These decompositions are due to the splitting off of HNO_2, $H_2S_2O_3$, or H_2CO_3, and to the volatility or instability of these acids.

The change of pH on merely diluting a solution may bring about a

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alcohol compound appears to have a marked ability to peptize hydrous ferric oxide. This involves the phenomena of colloid chemistry, which are discussed in Chapter X.

demasking in solutions of labile complex compounds. Instances are provided by barium sulfate and silver chloride. Their solutions in concentrated sulfuric acid and hydrochloric acid, respectively, or in concentrated solutions of their alkali salts, deposit $BaSO_4$ or $AgCl$ on dilution. In these cases, the complex $[Ba(SO_4)_2]^{--}$ or $[AgCl_2]^{-}$ ions are broken down into their components. The foregoing examples involve demaskings by lowering the pH. There are, however, complex ions which can be demasked by raising the pH. The ions $[Fe(CNS)_6]^{---}$, $[FeF_6]^{+++}$, $[AlF_6]^{---}$, $[ZrF_6]^{--}$, $[Fe(PO_4)_2]^{---}$, and $[Al(C_2O_4)_3]^{---}$, are in this category. They are stable only in acid solution and are decomposed on alkalization, with formation of hydroxide or phosphate. Obviously, a knowledge of the relation between a masking or demasking and definite pH values is of considerable analytical value. Special interest attaches to complex compounds that are stable over a wide range of acidity or alkalinity, and which accordingly are not demasked by considerable changes in pH. Unfortunately, very few such examples are known. As a rule, the analyst employs maskings in media that are either distinctly alkaline or acid.

The second type of demasking, to be considered here, is based not on a radical change of pH but on an entirely different type of effect. A scrutiny of the general equation of a reaction that results in a masking (see p. 67) leads to the following conclusion. A solution, in which a molecular or ionic species, A, is masked, will remain unaltered when a reagent for A is added, provided the reagent does not respond to the prevailing diminished (masked) concentration of A furnished by AMs. If a compound that reacts with the masking agent and thus consumes it is then added, prompt reaction will occur between the reactant A, liberated by the demasking, and the reagent for A that had been previously introduced. Feigl and Kapulitzas[95] applied this principle of demasking to qualitative analysis. They detected traces of nickel in cobalt salt as follows: A solution containing Co^{++} and Ni^{++} ions was treated with an excess of KCN and H_2O_2. The resulting soluble $K_2[Ni(CN)_4]$ and $K_3[Co(CN)_6]$ contain complexly bound nickel or cobalt, and give no response when dimethylglyoxime is added. If the test solution containing excess potassium cyanide and dimethylglyoxime is then treated with an excess of formaldehyde, the latter not only reacts with the free KCN to form glycolic nitrile, but it also withdraws cyanide ions from the masked system $[Ni(CN)_4]^{--}$ + dimethylglyoxime. The red Ni dimethylglyoxime compound precipitates as a result of this demasking. On the other hand, formaldehyde has no effect on the more stable $[Co(CN)_6]^{---}$ ions and leaves the cobalt in this form of combina-

[95] F. FEIGL and H. KAPULITZAS, *Mikrochemie*, Emich Festschrift **1930**, 120; *Z. anal. Chem.* **82**, 417 (1930).

tion where it is inactive toward dimethylglyoxime. It is thus possible to detect and determine traces of nickel in cobalt salts when the former are too slight to react on direct application of dimethylglyoxime because the reagent is all consumed by the Co^{++} ions. A similar selective demasking of complex cyanides by formaldehyde, with formation of glycolic nitrile, has been used in the system: $K_2[Cu_2(CN)_4] + K_2[Cd(CN)_4]$.[96] In alkaline solution, only the latter complex cyanide is demasked. The resulting $Cd(OH)_2$ can be detected by the formation of a color lake with diphenyl-carbazide, without any interference by the copper, which remains bound in the cyanide complex. Ubbelohde[97] found that a clear solution of $K_2[Ni(CN)_4]$ plus dimethylglyoxime can be used as reagent for those metal ions which form non-dissociating cyanides. The cyanide ions are taken away from the complex and the nickel is thus liberated. The latter can then react with the dimethylglyoxime in the normal manner. The formation of red Ni dimethylglyoximate will accordingly reveal small amounts of silver, mercury, and lead. Insoluble silver halides also bring about an analogous demasking through the formation of AgCN or $K[Ag(CN)_2]$. Hence, they too can be detected by a production of red Ni-dimethylglyoximate.[98] Demasking of the nickel in complex alkali nickel cyanides so as to render it accessible to the dimethylglyoxime reaction has been put to analytical use. Sanchez[99] found that when silver nitrate is added to a solution of $K_2[Ni(CN)_4] + K_3[Co(CN)_6]$ only the CN^- ions of the nickel compound are consumed, with production of AgCN and $Ni(NO_3)_2$. After removing the AgCN, the nickel in the filtrate can be precipitated by dimethylglyoxime. This same principle was applied later by Middleton and Miller[100] in the quantitative determination of nickel in the presence of large amounts of cobalt. The demasking of nickel in complex alkali nickel cyanides by means of the AgCN precipitation has the obvious disadvantages of requiring a filtration and of being interfered with by other anions that are precipitable by silver nitrate. The formaldehyde procedure (see p. 105) avoids the inconveniences accompanying the precipitation of silver cyanide and other halides. It is an excellent example of the advantages that can be secured by using organic reagents in inorganic analysis.

An interesting case of demasking an organic compound from an inner complex anion has been discovered and used by F. and H. E. Feigl.[100a] Alkali hydroxide solutions of Pd-dimethylglyoximate contain the water-soluble alkali salt of a complex acid (compare p. 276), in which the reac-

[96] P. KRUMHOLZ and F. HOENEL, *Mikrochim. Acta* 2, 277 (1937).
[97] A. R. UBBELOHDE, *Analyst* 69, 339 (1934).
[98] F. FEIGL, Laboratory Manual, p. 151; Spot Tests, p. 302.
[99] J. A. SANCHEZ, *Bull. soc. chim.* [4] 5, 641 (1909).
[100] A. R. MIDDLETON and H. L. MILLER, *J. Am. Chem. Soc.* 38, 1705 (1916).
[100a] F. FEIGL and H. E. FEIGL, *Anal. Chim. Acta* (in press).

tions of the palladium and the dimethylglyoxime of the complex anion are masked. Addition of alkali cyanide to such solutions produces $(Pd(CN)_4)^{--}$ ions with simultaneous release of the dimethylglyoxime. The latter can then be detected by adding Ni^{++} ions, which give an equivalent amount of the familiar red precipitate. In this manner, *i.e.*, through a demasking reaction, it is possible to detect cyanide specifically and with high sensitivity. In fact, it appears possible to base a gravimetric determination of cyanide on the weight of the Ni-dimethylglyoxime precipitate.

Another application of demasking is the detection of acidic materials by the production of insoluble red-brown silver chromate from the yellow aqueous solutions of $[Ag(NH_3)_2]_2CrO_4$ or $[Agen]_2CrO_4$. These solutions deposit Ag_2CrO_4 when the complex-forming ammonia or ethylenediamine molecules are withdrawn.[101] It is remarkable that amorphous silica is able to demask argentammine chromate. It obviously functions by adsorbing the ammonia or ethylenediamine. Crystalline and amorphous silica can be differentiated by this effect.[102] A further analytical application of demasking is found in a test for palladium, in which $Pd(CN)_2$ and red-violet Hg-diphenylcarbazide are formed from the system: $Hg(CN)_2$ + diphenylcarbazide.[103]

Some instances of demasking, which have been recognized and used in quantitative analysis, deserve particular notice. Böttger[104] has shown that Hg^{++} ions, because of their great tendency to form water-soluble, non-dissociating $Hg(CN)_2$, are able to decompose rapidly both soluble and insoluble normal and complex cyanides, such as copper ferrocyanide, Prussian blue, *etc.* A procedure for quantitatively determining halogens, by precipitation with silver nitrate in the presence of acid-stable complex cyanides, has been developed on this basis. Furman[105] has shown that the prevention of the SnS_2 precipitation from solutions containing fluoride ions (see p. 62) can be nullified by adding boric acid. This demasking and consequent liberation of Sn^{++++} ions, which can then be precipitated by H_2S, may be explained as follows. The BO_3^{---} ions withdraw F^- ions from the $[SnF_6]^{--}$ ions of the complex equilibrium, and form stable complex $[BF_4]^-$ ions:

$$[SnF_6]^{--} \rightleftharpoons Sn^{++++} + 6F^-$$
$$BO_3^{---} + 4F^- + 6H^+ \rightarrow [BF_4]^- + 3H_2O$$
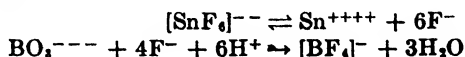
An analogous removal of fluorine by means of boric acid is possible in the fluorinated acids of molybdenum, tungsten and vanadium, in which, because of principal valence binding of the fluorine, there is a masking

[101] F. FEIGL and P. E. BARBOSA, *Ind. Eng. Chem., Anal. Ed.* **14,** 519 (1942).
[102] F. FEIGL, Laboratory Manual, p. 155.
[103] F. FEIGL, Laboratory Manual, p. 150; Spot Tests, p. 107.
[104] W. BÖTTGER, *Z. anal. Chem.* **48,** 356 (1909).
[105] N. FURMAN, *Ind. Eng. Chem.* **15,** 1071 (1923).

of the reactions of the MoO_4^{--}, WO_4^{--}, and VO_3^- ions. Compare footnote 77°.

Meigen and Schnerb[106] originated a method of breaking down complex aluminum tartrate ions so that the aluminum can be precipitated by ammonia. The tartaric acid is catalytically oxidized by hydrogen peroxide and copper salts (see p. 131). Probably this procedure could also be used to demask other complex metal tartrates.[107]

Only the most instructive of the many known examples of masking and demasking have been cited in this chapter. They show that these actions can be applied in analytical procedures to secure a variety of results: (1) Prevention of precipitation and color reactions through the use of strong masking agents; (2) Lowering of the concentration of an ionic species, by means of a weak masking agent, to such a degree that the masked system can function as a reagent;[108] (3) Use of masked reaction systems to detect a demasking agent; (4) Demasking of masked systems in order to liberate reactive ions for subsequent identification and determination.

A review of the chemical bases of the instances of masking and demasking cited in this chapter will reveal that many of these procedures involve reactions which lead to the formation or decomposition of complex compounds. This situation presents an especially attractive province of applied complex chemistry, a branch which has already rendered such valuable aid to analytical chemistry, and which promises to continue to give fruitful results in efforts directed toward increasing the selectivity of identification tests and quantitative methods, and, where possible, to raise these to specificity. However, as pointed out in this chapter, other effects can also serve as the basis of the masking of reactions and they too should be considered in investigations directed toward the attainment of new or better tests.

[106] W. MEIGEN and J. SCHNERB, *Z. angew. Chem.* **37**, 208 (1924).

[107] This procedure was selected for inclusion here primarily to illustrate the principle of demasking, and not because of its practical usefulness. At the time of its publication it presented a really brilliant solution of a difficult analytical problem. The great advantage of using the methods of complex chemistry in analytical chemistry, and also the closely related action of organic reagents, is exemplified by the now common use of oxine to detect and determine aluminum, iron, *etc.*, in masked solutions (see p. 185). This problem formerly was most difficult. Many metal oxinates have such small solubility products that the minute concentrations of metal ion available in masked alkaline solutions are still adequate to produce a quantitative precipitation when oxine is added.

[108] The use of weak masking agents to reduce an ionic concentration in order to provide more favorable precipitation conditions in gravimetric procedures, will be discussed in Chapter XI.

Enhancement of Reactivity of Compounds and Reaction Systems

The examples cited in Chapter IV of hindered reactions in aqueous solutions have a common basis: the reduction of the concentration of an ionic or molecular species by binding it into a soluble complex compound or into an abnormally dissociating principal valence compound by union with constituents of the masking agent. The reverse cases in which the extent of a reaction or the reaction velocity of a system is increased are of no less analytical importance with regard to specificity, selectivity, sensitivity, and elimination of sources of error. The relevant phenomena can be discussed under several captions.

Raising the Reactivity by Complex Formation

The precipitation of stannic sulfide from stannic solutions can be prevented by phosphoric, oxalic, or hydrofluoric acid (see p. 82). Conversely, precipitated SnS_2 is easily brought into solution by these acids. If consideration is limited to the action of the hydrogen ion, only as much SnS_2 can be taken into solution as corresponds to the equilibrium position of the reversible reaction:

$$SnS_2 + 4H^+ \rightleftharpoons Sn^{++++} + 2H_2S \tag{1}$$

In view of the quantitative precipitability of stannic sulfide in acid solution, this equilibrium lies far toward the left. However, it is constantly disturbed if oxalate, phosphate, or fluoride ions are present, since they remove the stannic ion through complex formation, as for example,

$$Sn^{++++} + 6F^- \rightleftharpoons [SnF_6]^{--}$$

or

$$Sn^{++++} + 3C_2O_4^{--} \rightleftharpoons [Sn(C_2O_4)_3]^{--}$$
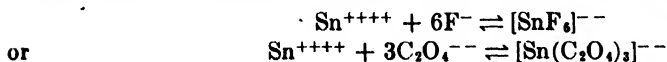
which necessitates the constant replenishing of stannic ions. This continues until all the stannic sulfide has disappeared.

The anomalous acid-solubility of stannic sulfide in the presence of complex-formers exemplifies the fact that the reactivity of a material can be raised in a particular direction by the formation of a complex compound. This presents a phenomenon that is the opposite of reaction masking. Abnormal solubilities are often due to the disturbance of equilibria because of complex formation. The following example illustrates how this may be of analytical importance.

Natural calcium fluoride is only slightly soluble in water or in dilute acids, since the positions of the equilibrium:

$$\underset{\text{(solid)}}{CaF_2} \rightleftharpoons Ca^{++} + 2F^-$$
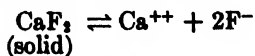
lie chiefly toward the left and cannot be markedly shifted by diluted acids. Only by treatment with concentrated acids and heating is the weakly dissociated and volatile HF formed in such amounts that complete solution of the CaF_2 can occur. However, this equilibrium between CaF_2 and its ions can also be disturbed with diluted acids, if the fluoride ions are removed—an easy matter since fluoride ions enter readily into complexes. In fact, calcium fluoride, when gently warmed, dissolves with great ease in dilute acids if aluminum, ferric, beryllium, or zirconium salts are present, since the respective fluometallic acids with the ions $[AlF_6]^{---}$, $[FeF_6]^{---}$, $[BeF_4]^{--}$, or $[ZrF_6]^{---}$ are formed. Boric acid also favors the solution of calcium fluoride because of the production of complex fluoboric acids. For instance, if calcium fluoride is dissolved in dilute acid in the presence of beryllium salts, the calcium can be quantitatively precipitated as oxalate, after buffering the free mineral acid by acetate.[1]

The ease of forming the complex $[ZrF_6]^{--}$ ion and its stability are the basis of a very sensitive test for fluoride[2] as well as of a volumetric method for determining this element.[3] The deep red zirconium alizarinate, in acid solution, reacts with solid and dissolved fluorides to produce the colorless $[ZrF_6]^{--}$ ion and free alizarin; the color changes from red to yellow (the color of free alizarin).

Complex formation can thus increase the solubility of materials if one constituent of the precipitate is removed from the equilibrated system. Likewise, the reducing or oxidizing action of a compound can be increased by complex binding of the resultant oxidized or reduced stage, since the equilibrium is then shifted to favor the end products. For instance, iodine is only partially reduced to iodide ion by ferrous salts:

$$I_2 + 2Fe^{++} \rightleftharpoons 2I^- + 2Fe^{+++}$$
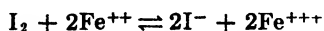
but the reaction becomes practically complete if a complex-former for Fe^{+++} ion, such as phosphate or fluoride, is added. An exact measure of the reducing or oxidizing power of a material is given by its oxidation-reduction (redox) potential, whose value is determined, in part, by the relative molar concentrations of the oxidized and reduced stages. The reducing power of ferrous salts, for example, is increased (that is, their reduction potential is higher) if the ferric salts that are originally present or that are produced by the oxidation are removed. This removal of ferric ions is accomplished readily by means of masking agents. Such

[1] F. FEIGL, unpublished studies with G. HIRSCH, Dissertation, Vienna, 1921; compare F. FEIGL, *Z. angew. Chem.* **42**, 212 (1929).

[2] F. FEIGL, Spot Tests, p. 203.

[3] J. DE BOER and J. BASART, *Z. anorg. allgem. Chem.* **152**, 213 (1926).

strengthening of the reducing action of ferrous solutions is shown easily[4] if they are treated with a yellow solution of cacotheline, which is a nitro compound of the alkaloid brucine. The mixture remains unchanged even after standing for several hours, but it immediately turns deep violet if a fluoride or phosphate is introduced into the acid solution. The violet coloration is due to a reduction product of cacotheline;[5] it forms only when the reducing potential of the ferrous salt is raised by masking the ferric ion. For the same reason, even a ferrous salt that by itself has no action on solutions of methylene blue, or tellurite, or palladous chloride, will (on warming) react, with precipitation of tellurium or palladium, if phosphoric acid or fluoride is added.[6a] Kurtenacker and Kubina[6b] described a nice application of the increased reducing action of ferrous salts. The reaction:

$$S_2O_8^{--} + 2Fe^{++} \rightarrow 2SO_4^{--} + 2Fe^{+++}$$
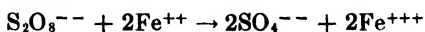
through back titration of the unused Fe^{II} with $KMnO_4$, provides the basis of a titrimetric method of determining persulfate. However, at room temperature and with no more than slight excess of Fe^{II}, the reaction is sluggish and the method is not satisfactory. The addition of phosphoric acid makes the reaction proceed instantly and quantitatively.

In the foregoing examples, the reducing action of ferrous salts was enhanced by binding, in phosphate or fluoride complexes, the ferric ions formed during the reaction. Instances are also known in which oxidizing actions are intensified by removing the reduction products. Soluble cupric salts normally are weak oxidants; they are not capable of oxidizing benzidine to benzidine blue (see p. 335). The equilibrium: Cu^{II} + benzidine $\rightleftharpoons Cu^I$ + benzidine blue, because of the pronounced reducing action of Cu^I, does not lie far enough toward the right to permit the perceptible production of benzidine blue. If, however, benzidine is treated with a Cu^{II} salt in the presence of Br^-, I^-, or CNS^- ions, the univalent copper is removed by formation of an insoluble cuprous salt. If CN^- ions are present, a soluble complex is produced. The oxidizing potential of the cupric salts is thus heightened in all of these cases. Practical sensitive tests for copper[7] and for cyanide[8] have been based on this shift of the equilibrium. A similar rise in the oxidation potential of ferricyanide has been applied in a method for detecting zinc.[9] This

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[4] F. FEIGL, unpublished studies.

[5] F. FEIGL, Spot Tests, p. 87.

[6a] F. FEIGL, unpublished studies.

[6b] A. KURTENACKER and H. KUBINA, Z. anal. Chem. **88**, 14 (1931).

[7] F. FEIGL and F. NEUBER, Z. anal. Chem. **62**, 375 (1923).

[8] A. SIEVERTS and A. HERMSDORF, Z. angew. Chem. **34**, 3 (1921).

[9] E. EEGRIWE, Z. anal. Chem. **74**, 228 (1928).

test makes use of the fact that hydroferricyanic acid can oxidize diethyl-aniline and other aromatic amines, and also monoazo dyes.[10] Ferro-cyanide is formed along with the colored oxidation products. However, these oxidations proceed slowly and incompletely because the resulting ferrocyanide is a strong reducing agent and arrests the reaction. If zinc ions are also present, insoluble zinc ferrocyanide precipitates and the ferrocyanide is thus removed from the redox system. The oxidation, under such circumstances, proceeds rapidly, and the zinc ferrocyanide precipitate acquires a characteristic color. Very small quantities of zinc can be detected in this way, if, for instance, the oxidation of diethyl-aniline is carried out in phosphoric or sulfuric acid solution.

In the foregoing examples an increased reactivity was obtained by shifting equilibrium of the system through removal of a reaction product. It is likewise possible to alter decidedly the dissociation equilibrium of a weak electrolyte by incorporating it in a complex combination. Under certain circumstances, the concentration of a particular kind of ion is thus so greatly raised that reactions, not shown by the original com-pounds because of insufficient dissociation, become possible. This is the converse of reaction masking, in which the concentration of an ionic species is decreased so greatly through complex formation that a reaction, which otherwise would normally be expected, does not occur.

A very clear case of the increase of the degree of dissociation through complex formation is the *rise in the acidity* of compounds, which of them-selves furnish only slight concentrations of hydrogen ion. Water dis-sociates to only a minute extent into hydrogen and hydroxyl ions. The coordination of water with certain metal salts, however, produces strong acids. For example, the hydrate of auric chloride, $H[AuCl_3OH]$ is a very strong acid. Meerwein[11] found that a concentrated water solution of zinc chloride, in which the compound $H[ZnCl_2OH]$ is present, also displays a strong acid reaction; *e.g.*, it dissolves metals with liberation of hydrogen. Hydroferro- and hydroferricyanic acids are quite strong acids. They likewise can be regarded as coordination compounds of iron cyanides with the weak hydrocyanic acid, and hence a considerable increase in the strength of the latter acid results from the coordination. The increased acidity can obviously be ascribed to the fact that the coordination of the oxygen atom of the water molecule, or of the cyanide group in the prussic acid molecule, leads to a weakening of the hydrogen linkage, and eventually results in a complete splitting off of the hydrogen ions.

[10] W. H. Cone and L. C. Cady, *J. Am. Chem. Soc.* **49**, 2214 (1927).

[11] H. Meerwein, *Ann.* **455**, 227 (1927); cf. also F. Reiff, *Z. anorg. allgem. Chem.* **206**, 321 (1931).

Another instance of the raising of acidity through complex formation is the "activation" of boric acid. It has long been known[12] that the presence of polyhydric alcohols, such as mannitol or glycerol (or other hydroxyl or carboxyl compounds), causes the extremely weak boric acid to function as a monobasic acid of such strength that it liberates carbon dioxide from carbonates, and can be titrated, with phenolphthalein as indicator. The esterlike compounds of boric acid, such as the pinacone compound, show no increase in the acidity. However, compounds that contain the boron linked in an inner complex, glycol-boric acid for instance, are medium strong acids. In general, increased acidity of boric acid appears to be brought about only by such compounds as contain two carboxyl or hydroxyl groups so situated that the formation of stable inner complex rings is possible.[13] The formulation of the glycolic acid compound as

$$\left[\begin{array}{cc} H_2CO & OCO \\ | & | \\ & B \\ | & | \\ OCO & OCH_2 \end{array} \right] H$$
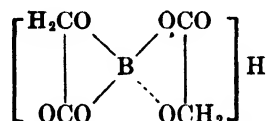
shows that the increase of acidity really does not concern the boric acid itself, but involves rather an hydroxyl group of the organic component, which, through the coordination of the oxygen atom on the boron, leads to the separation of the hydrogen atom in the ionogenic form. These examples of increase in acidity can be appropriately termed alteration of function by complex formation. The extent of the increase in acidity of boric acid by mannitol was studied by Treadwell and Weiss.[14] The potentiometric titration curve of boric acid in the presence of mannitol indicates a dissociation constant for mannitol-boric acid of 6.3 to 8.4×10^{-6}, while the dissociation constant of pure boric acid is 6×10^{-10}. Hahn[15] used the increase in acidity of boric acid brought about by glycerol or mannitol to detect, through indicator changes, minimal quantities of boric acid.[16]

Phenylboric acid, $C_6H_5B(OH)_2$, behaves like boric acid; it also can be titrated if glycerol is present.[17] Rosenheim and Weinheber,[18] found the

[12] J. BIOT, Compt. rend. 14, 49 (1842).

[13] The numerous comprehensive studies of J. Böeseken concerning the compounds of boric acid with organic materials containing OH and CO are discussed in Chapter VI.

[14] W. TREADWELL and L. WEISS, Helv. Chim. Acta 3, 440 (1920).

[15] F. HAHN, Compt. rend. 197, 762 (1933).

[16] F. FEIGL, Spot Tests, p. 260.

[17] G. BRANCH and D. JABROFF, J. Am. Chem. Soc. 54, 2569 (1932).

[18] A. ROSENHEIM and A. WEINHEBER, Z. anorg. allgem. Chem. 69, 266 (1911).

same is true for telluric acid, and Tschakirian[19] showed that germanic acid likewise forms with glycerol, glucose, or mannitol, a strong monobasic complex acid that can be titrated with alkali in the presence of phenolphthalein.[20]   The acidity of arsenic acid can be raised by mannitol or sorbitol.[21]

The acidity of tartaric, citric, and malic acids can likewise be enhanced through complex formation.   These acids cannot be determined iodometrically on the basis of the reaction:

$$6H^+ + IO_3^- + 5I^- \rightarrow 3H_2O + 3I_2$$
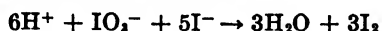
because the H^+ ion concentration is too low at the end of the titration. However, if calcium, magnesium, or zinc salts are added, the iodometric determination of these hydroxy acids becomes possible.[22]

Instances of *increase of alkalinity* because of complex formation are also known.   Thus, $[Ag(NH_3)_2]OH$ and $[Cu(NH_3)_4](OH)_2$ and other metal hydroxide-ammoniates are stronger bases, because of the addition of ammonia, than either the parent metal hydroxide or ammonium hydroxide.

Weak electrolytes, other than acids or bases, can similarly be made to undergo an increase in dissociation through coordinative linkage.   The compound $Hg(CN)_2 \cdot KOH \cdot H_2O$[23] produced from mercuric cyanide and alkali is a good example.   This compound was described and thoroughly investigated by Hofmann and Wagner.[24]   Mercuric cyanide is soluble in water, but ionizes only slightly.   The concentration of cyanide ion is so small that the addition of silver ion causes no precipitation of silver cyanide, even though a minute concentration of cyanide ion normally suffices for this test.   If, however, the solution is treated with only a few drops of potassium hydroxide solution (of course no mercuric oxide precipitates), the clear solution immediately precipitates $AgCN$ on the addition of silver ion.   Consequently, the alkali has caused the mercuric cyanide to deliver considerable quantities of cyanide ion.   The reason is the formation of the complex compound $Hg(CN)_2 \cdot KOH \cdot H_2O$, to which the coordination formula:

[19] A. Tschakirian, *Compt. rend.*, **187**, 229 (1928).

[20] N. Poluektoff, *Z. anal. Chem.*, **105**, 24 (1936).

[21] F. Auerbach, *Z. anorg. allgem. Chem.*, **37**, 353 (1903).   Compare B. Englund, *Rec. trav. chim.*, **51**, 135 (1932).

[22] I. M. Kolthoff, *Z. anal. Chem.*, **60**, 456 (1921).

[23] The corresponding NaOH as well as the alkali alcoholate compounds are known. Their ease of formation is indicated by the fact that the solubility of $Hg(CN)_2$ in water is raised considerably by alkalies, and just as much by KOH as by NaOH. Compare R. Weinland, Einführung in die Chemie der Komplexverbindungen, 2nd ed. p. 258.   Stuttgart, 1924.

[24] K. Hofmann and H. Wagner, *Ber.* **41**, 1628 (1908).

$$K \begin{bmatrix} CN & & CN \\ & Hg & \\ H_2O & & OH \end{bmatrix}$$
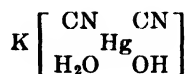
may be assigned.[25] It dissociates:

$$K[Hg(CN)_2(H_2O)(OH)] \rightleftharpoons K^+ + [Hg(CN)_2(H_2O)(OH)]^-$$
$$[Hg(CN)_2(H_2O)(OH)]^- \rightleftharpoons Hg(CN)(OH) + H_2O + CN^-$$
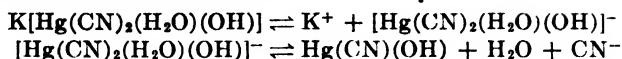
and the cyanide ion concentration then reaches a value at which the solubility product of silver cyanide can be exceeded. The production of cyanide ions from mercuric cyanide is, therefore, the result of the formation and dissociation of the complex anion $[Hg(CN)_2(OH)(H_2O)]^-$, which is formed:

$$Hg(CN)_2 + OH^- + H_2O = [Hg(CN)_2(OH)(H_2O)]^-$$
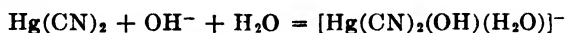
The formation of this complex anion and its dissociation furthermore exemplify not only the raising of the reactivity of the mercuric cyanide but also an interesting displacement· of cyanide ions. When sodium hydroxide is added to a solution of mercuric cyanide, the hydroxyl ions disappear almost completely and cyanide ions take their place.

The foregoing examples show that the degree of dissociation of compounds can be increased by complex formation. Occasionally, a more rapid oxidizability or reducibility can be attained by incorporating a compound in a complex. Complex formation of this type, in contrast to the examples of equilibrium shifts given earlier, directly influence the reaction velocity of a system. A typical example is the behavior of the heteropoly acids of molybdenum of the type $H_3PO_4 \cdot 12MoO_3$. Acidified molybdate solutions liberate iodine to only a small extent from potassium iodide. Likewise, they oxidize ferrous salts, sulfurous acid, phenylhydrazine hydrochloride, benzidine, or potassium ferrocyanide only incompletely and very slowly, and convert aniline to aniline black to only a slight extent. In these cases, beside the respective oxidation products, molybdenum blue[26] is always formed as a reduction product of the molybdic acid. The progress of the oxidation, or of the reduction, can be followed easily by the deepening in color of the molybdenum blue formed, or by the change in color of the solution in case the oxidation product is also colored. If the foregoing reducing agents are used, the production of molybdenum blue from molybdates proceeds very slowly. In contrast, the reduction is quite rapid if a trace of phosphoric acid (which forms the heteropolyacids) is added.[27]

This greater ease of reducing MoO_3 that is complexly bound in phos-

[25] Compare F. FEIGL and J. TAMCHYNA, *Ber.* **62**, 1897 (1929).

[26] For literature concerning molybdenum blue compare S. MALOWAN, *Z. anal. Chem.*, **84**, 209 (1931); R. RINNE, **113**, 241 (1938). *ibid.*

[27] Compare A. TAYLOR and C. MILLER, *J. Biol. Chem.* **18**, 215 (1914).

phomolybdic acids has been applied in various ways in spot test analysis. Feigl and Neuber[28] used it as the basis of a test for copper, in which cuprous cyanide formed from Cu^{++} and CN^- ions reacts with phosphomolybdic acid to produce molybdenum blue. They also recommended phosphomolybdic acid as a reagent for divalent tin and trivalent antimony, and pointed out that the acid-insoluble ammonium phosphomolybdate reacts only with Sn^{II} but not with Sb^{III}, thus making possible the detection of tin in the presence of antimony. Phosphomolybdic acid has been recommended as a general reagent for reducing agents, i.e., for both soluble and insoluble inorganic and organic reductants.[29] It is important as regards the analytical applicability of the easier reducibility of molybdenum in phosphomolybdic acids that not only the free acid and the acid-stable ammonium salt can participate in redox reactions at low pH values, but that, in addition, redox reactions can take place when the acid and the ammonium salt are made alkaline in the presence of a readily oxidizable material. This seems astonishing at first glance, because ammonia, alkali hydroxide, carbonate, or acetate, are known to decompose phosphomolybdic acid and its acid-stable salts, splitting the complex compounds into alkali phosphate and molybdate. Hence, it must be assumed that, when a particular pH value is reached during the course of the alkalization, the complex anion can enter into redox reactions and that the redox reaction proceeds faster than the splitting of the complex. A test for phosphate developed by Feigl[30] should be viewed in this sense. The procedure is to moisten a precipitate of $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot aq$ with benzidine and then hold it over ammonia, or treat it with sodium acetate. A deep blue appears. This color is due to the simultaneous production of oxidized benzidine (benzidine blue) and reduced molybdenum (molybdenum blue). The test is so sensitive that amounts of ammonium phosphomolybdate that are even too small to be seen with the naked eye are made manifest by the development of the blue color. West and Houtmann[31] showed that strychnine phosphomolybdate, formed from a mixture of strychnine sulfate, molybdic acid, and phosphate, behaves similarly to ammonium phosphomolybdate toward benzidine and alkalinization. The preceding discussion indicates why, on alkalinization, acid-insoluble salts of phosphomolybdic acid with easily oxidized bases, may undergo a redox reaction that involves both the cationic and anionic component of the salt. For instance, in acid solution, benzidine, and likewise 8-hydroxyquinoline,

[28] F. FEIGL and F. NEUBER, Z. anal. Chem. **62,** 376 (1923).
[29] F. FEIGL and G. DACORSO, Chemist-Analyst **32,** 28 (1943).
[30] F. FEIGL, Z. anal. Chem. **61,** 454 (1922); **74,** 386 (1928); **77,** 299 (1929).
[31] P. W. WEST and T. HOUTMANN, Ind. Eng. Chem., Anal. Ed. **14,** 597 (1942).

produce yellow phosphomolybdate precipitates that immediately turn blue when made alkaline. In the case of the benzidine compound, the redox reaction can be brought about on merely washing the precipitate with water to remove the free acid. The redox reactions of phosphomolybdic acid in the alkaline range also include the fact that the autoxidizable hydrated oxides of Mn^{II}, Co^{II}, and Ce^{III} react promptly with phosphomolybdic acid in the presence of fixed alkalies with production of the respective higher metal oxyhydrates and molybdenum blue. Komarowsky and Korenmann[32] used this finding as the basis of a very sensitive spot reaction for cerium. The test is strictly specific within the group of rare earths. The following observation by Poluektov[33] merits particular emphasis in connection with the activation of the molybdenum in complex phosphomolybdates. The reaction can be used as a spot test for thallium. If a drop of a solution of a thallium salt and one drop of an aqueous solution of. phosphomolybdic acid are placed on filter paper and spotted with a strong solution of hydrobromic acid, a fleck of molybdenum blue appears. The color intensity depends on the quantity of thallium present. Since phosphomolybdic acid does not react with hydrobromic acid at room temperature, Poluektov assumed that the spatial proximity of the oxidizable Tl^{I} and of the reducible Mo^{VI} is decisive for the occurrence of the redox reaction. Accordingly, this would be a topochemical reaction (see Chapter XI). Though this hypothesis may be valid, the author believes that the following additional explanatory points should be kept in mind. The complexly bound MoO_3 of the phosphomolybdic acid may react with hydrogen bromide:

$$2MoO_3 + 2HBr \rightleftharpoons H_2O + Mo_2O_5 + Br_2$$
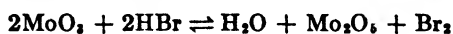
This reaction takes place vigorously when the temperature is raised, but at room temperature it probably comes to an equilibrium that lies so slightly toward ·the right that no production of molybdenum blue is visible. If, however, Tl^{I} is introduced into this system, it functions as an acceptor for the free bromine: $Tl^+ + Br_2 \rightarrow Tl^{+++} + 2Br^-$. Hence, the removal of the free bromine may lead the redox reaction between MoO_3 and HBr to proceed to lengths that it cannot attain unless the equilibrium is constantly disturbed. This viewpoint is strengthened by the fact that the reaction between phosphomolybdic acid and hydrobromic acid is initiated by Hg_2Cl_2 or Sb^{III} salts,[34] as well as by thallous salts, i.e., by compounds which, like the latter, can function as acceptors for free bromine. Consequently, this instance involves

[32] A. S. KOMAROWSKY and J. M. KORENMANN, *Mikrochemie* 12, 211 (1932).
[33] N. S. POLUEKTOV, *Chem. Zentr.* 1934 [I], 3420.
[34] F. FEIGL and I. D. RAACKE, unpublished studies.

an interesting combination of two kinds of reaction enhancement: (a) activation of Mo^{VI} through complex binding, which however is not sufficient to bring about, at room temperature, oxidation of hydrogen bromide in quantities large enough to be detected directly; (b) accomplishment of an extensive oxidation of hydrogen bromide as the result of the taking-up of free bromine by Tl^{I}, Hg_2Cl_2, or Sb^{III}. As end-effect, the redox reaction between Tl^{I}, Sb^{III}, or Hg_2Cl_2 and phosphomolybdic acid, which of itself occurs not at all or at an immeasurably slow rate, is brought to rapid occurrence by the insertion of hydrogen bromide, or of the bromine to which it gives rise, into the redox reactions with Mo^{VI} and Tl^{I}. This is a reaction mechanism of the type of intermediate reaction catalysis to be discussed later. However, in most cases, even very small amounts suffice for the activity of a catalyst, but in this instance the catalytically active hydrobromic acid must be present in considerable concentrations.

The ease of reducing the molybdenum is due solely to the coordination of the molybdenum trioxide. This is also shown by the fact that the molybdenum in the arseni-, silico-, and germanimolybdic acids (analogous to the phosphorus compound) is likewise easily reduced by benzidine. These heteropolyacids patently possess analogous linkings with respect to their molybdenum trioxide molecules, despite the difference of the central atoms (P, As, Si, Ge). The induction of the molybdic acid reaction by the complex formation with the MoO_3 molecules therefore makes possible, in addition to the phosphate test already mentioned, a test for silica.[35] This is so sensitive that it reveals the traces of SiO_2 dissolved by distilled water after standing for several hours in glass vessels, or derived from the glass by briefly boiling (1 minute) 10 ml. of water in a test tube.[36] Komarowsky and Poluektoff[37] have described a test for germanium which likewise is based on the enhanced oxidizing power of molybdenum (toward benzidine) in the complex germanimolybdic acid.

There are numerous heteropolyacids of molybdenum with phosphoric and arsenic acids. Strangely enough, there is an increase of the reactivity of the molybdenum only in the "twelve" acids.[38] In solutions that contain excess phosphoric acid and consequently lower heteromolybdates, there is even a restraint in the reactivity of the MoO_3, toward hydrogen iodide, for instance. The complex "twelve" acid, $H_3PO_4 \cdot 12MoO_3$, is reduced to a heteropolyacid of quinquevalent molyb-

[35] F. FEIGL, Spot Tests, p. 252.

[36] F. FEIGL and P. KRUMHOLZ, Ber. **62**, 1139 (1929).

[37] A. S. KOMAROWSKY and N. S. POLUEKTOFF, Mikrochemie **78, 66** (1935).

[38] P. KRUMHOLZ, Z. anorg. allgem. Chem. **212**, 97 (1933).

denum, probably $H_3PO_4 \cdot 10MoO_3 \cdot Mo_2O_5$. This compound can react with excess MoO_3, and so to a slight degree regenerate $H_3PO_4 \cdot 12MoO_3$. Consequently, if a solution containing a little phosphoric acid is treated with excess molybdate and then with a reducing agent such as potassium iodide, a quantity of "twelve" acid equivalent to the phosphoric acid, will first be reduced rapidly to the complex acid of quinquevalent molybdenum. However, since the latter reacts with molybdenum trioxide to regenerate the reactive "twelve" acid, the acceleration of the reaction does not cease completely with the stoichiometric reduction of the "twelve" acid present originally, but continues, though with diminished velocity, until all of the MoO_3 is reduced. Consequently, a small quantity of phosphoric acid is capable of accelerating (catalyzing) the reaction of a considerable quantity of MoO_3 with KI.

Enhanced reactivity due to complex binding is responsible for an interesting effect exerted by selenium on redox reactions between alkali sulfide and water solutions of methylene blue, fuchsine, picric acid, dipicrylamine, cacotheline, and potassium chromate.[39] The two dyes are reduced to the corresponding colorless leuco compounds, the nitro compounds to the respective red and violet amino derivatives, and the chromate to chromic hydroxide. These reactions, whose occurrence is readily apparent because of the resultant color changes or formation of precipitate, are decidedly accelerated by selenium. This effect is easily observed if concentrations are chosen at which the unaccompanied sulfide reacts slowly. The following simple experiment illustrates the marked effect of selenium on the reduction of methylene blue. A stock solution is prepared by dissolving 3 g. $Na_2S \cdot aq$ and 25 mg. selenium in a little water and then diluting to 100 ml. A duplicate sulfide solution, but containing no selenium, is prepared for comparison. Portions of the two solutions are diluted to 10, 20, 40, 80, *etc.*, times the original volume, and 1 ml. portions of each of these dilutions is taken for the actual test. Two drops of 0.15% methylene blue solution are added to each. The acceleration due to selenium is directly observable up to 1:400. At higher dilutions, up to 1:2,000, which corresponds to 0.13γ Se/ml., the activity can be plainly detected if a supplementary drop of 20% Na_2S solution is added before introducing the methylene blue.

The effect of the selenium probably is due to the fact that it dissolves in sodium sulfide solution and forms $[S \ldots Se°]^{--}$ ions. This coordination of selenium on sulfide ions raises their reduction potential. When methylene blue is reduced, free selenium and sulfur result, and both dissolve in the excess sodium sulfide. Consequently, the active $[S \ldots Se°]^{--}$ ions are regenerated. This explanation is supported by the fact that the

[39] F. FEIGL and P. W. WEST, *Anal. Chem.* **19**, 351 (1947).

action can be completely stopped by adding potassium cyanide, because potassium selenocyanide, KCNSe, is produced instead of $[S \ldots Se°]$ ions. There is the further possibility that the complex ion $[S \ldots Se°]^{--}$ is in equilibrium with its isomeric form $[Se \ldots S°]^{--}$. Even though the equilibrium: $[S \ldots Se°]^{--} \rightleftharpoons [Se \ldots S°]^{--}$ is shifted strongly toward the left, a more rapid reduction is still possible if the Se^{--} ion reacts more quickly than the S^{--} ion. The designation "increase of reactivity due to complex binding" is also justified here because the primary formation of the complex ion $[S \ldots Se°]^{--}$ is indubitably necessary. Further corroborative evidence is that the reduction of methylene blue is hastened also by the solution of a great deal of sulfur in sodium sulfide, to produce polysulfide. However, the action of sulfur is incomparably less than that of an equivalent quantity of selenium. Accordingly, coordination can be held responsible for this quite selective action of selenium, which permits analytical applications.[40]

The writer believes that an analogous explanation may logically be proposed for the catalytic effect of selenium in Kjeldahl digestions. This advance is due primarily to Lauro,[41] who found that selenium shortens the time required for the destruction of the organic matter by concentrated sulfuric acid and for the conversion of organically bound nitrogen into ammonium sulfate. His suggestion has been widely adopted.[42] Selenium dissolves in concentrated sulfuric acid. The green solution contains $Se°·SO_3$ (see p. 38) and it is very probable that the coordination of selenium on sulfur trioxide activates the latter and thus plays a decisive role in the dehydration and oxidative processes of the Kjeldahl digestion.

A fine example of another type of increasing reactivity by means of complex formation is the action of iodine on silver saccharinate suspended in various organic solvents.[43] Iodine dissolves in organic solvents

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[40] It is noteworthy, in this connection, that the activation due to sulfur is completely eliminated by adding Na_2SO_3 and warming. This removes the sulfur, as evidenced by the discharge of the color of the polysulfide solution, and forms thiosulfate. Alkali sulfide solutions that contain selenium are likewise decolorized by Na_2SO_3, but the production of Na_2SSeO_3 is incomplete and reversible, because the activation of seleniferous alkali sulfide solutions toward methylene blue is not nullified by adding alkali sulfite. Accordingly, as little as 0.5γ selenium can be detected in the presence of 24,000 times as much sulfur when these free elements are present in alkali sulfide solutions (compare note 39).

[41] M. F. LAURO, *Ind. Eng. Chem. Anal. Ed.* **3**, 401 (1931).

[42] A survey of the literature concerning the practical use of selenium as accelerator in the Kjeldahl procedure is given in W. W. SCOTT, Standard Methods of Chemical Analysis, 5th ed., p. 634, 2493. New York, 1939.

[43] F. FEIGL and E. CHARGAFF, *Monatsh.* **49**, 417 (1928); F. FEIGL and A. BONDI, *ibid.* **53–54**, 508 (1929).

to produce sometimes brown, sometimes violet solutions. The iodine has a greater reactivity toward the silver saccharinate suspended in the brown solutions than in the corresponding violet solutions. Under comparable conditions, silver iodide is produced·almost quantitatively from silver saccharinate in a brown solution (*e.g.*, ether), whereas in violet solution (*e.g.*, carbon disulfide) only a few percent of the possible silver iodide is formed.[44] Birkenbach and Linhard[45] observed the same effect with silver cyanate.[45a] An addition of small quantities of those materials that turn violet iodine solutions brown (*e.g.*, benzyl sulfide) makes these solutions likewise capable of producing considerable quantities of silver iodide from silver saccharinate. This increase of the reactivity of iodine is clearly due to the fact that the brown iodine solutions contain molecular compounds, composed of iodine and the solvent (solvates), or of iodine and molecules of the added activator. Iodine is in a more reactive state in these complex compounds. The catalytic character of this reaction, which is accelerated by complex formation, appears plainly because the catalyst produces a complex compound only with the starting material, but not with the end product of the reaction, as is the case with the heteromolybdates. A combination with the end product to produce a complex would incapacitate the catalyst severely. The next section will include a number of catalysis reactions which probably have a mechanism analogous to that just given. They can be termed "complex catalyses."

The preceding studies of the action of iodine on silver saccharinate suspended in organic liquids were undertaken ·in the hope that the elimination of silver iodide would lead to the formation of a hitherto unknown cyclic substituted hydrazine. The effort failed, and identity of the resulting reaction products has not yet been definitely ascertained. Prevost[46] was more successful in his investigation of the action of iodine on silver benzoate. Two moles of this silver salt reacted with iodine in benzene solution to produce $(C_6H_5COO)_2AgI$. Remarkably enough, this compound is quite soluble in benzene, and the pure solid can be

[44] This same difference in the behavior of brown and violet iodine solutions has been established in the reaction of iodine on diazoacetic ester. This reaction, occurring in a homogeneous system, is light-sensitive, and proceeds extremely slowly in the dark. Hence, if carried out in the light, this is an instance of double activation: (a) of iodine by solvation and (b) of the diazo compound by light. F. FEIGL and V. BERMANN, Dissertation of V. Bermann, Vienna, 1930.

[45] L. BIRKENBACH and M. LINHARD, *Ber.* **63,** 2545 (1930); see also L. BIRKENBACH and J. GOUBEAU, *ibid.* **65,** 398 (1932).

[45a] AgI and CNI are produced. The latter attaches itself to carbon double bonds. A selective test for cyanic acid has been developed from this action. A. LINHARD and M. STAPHAN, *Z. anal. Chem.* **88,** 16 (1932).

[46] C. PREVOST, *Compt. rend.* **196,** 1129 (1933).

isolated by crystallization from this solvent. The compound is not only a strong oxidizing agent toward organic and inorganic compounds, but it also reacts in a characteristic way with ethylene compounds. Silver iodide is split off, and two C_6H_5COO groups join to each of the two carbons of the $\diagdown C{=}C\diagup$ group. When saponified, these products yield the corresponding α-glycols. The writer believes that the benzene-soluble silver compound can be regarded as a complex compound between benzoyl superoxide and silver iodide:

$$\begin{matrix} C_6H_5COO \\ | \\ C_6H_5COO \end{matrix}\Big\rangle AgI \quad \text{or} \quad \left[\begin{matrix} C_6H_5COO \\ | \\ C_6H_5COO \end{matrix}\Big\rangle Ag\right] I$$
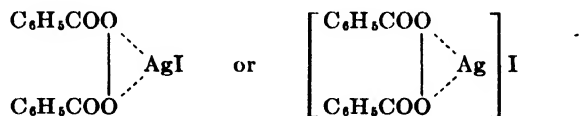
Since benzoyl superoxide, *per se*, is not more than a weak oxidant, and under like conditions is not capable of addition on ethylene compounds, this is a nice example of the enhancement of the reactivity of an organic compound through complex formation. It is likely that the benzene solution of the complex silver compound may also have some analytical use, since its reactions with reactive ethylene compounds produce silver iodide, which even in small amounts gives a visible turbidity.

CATALYZED REACTIONS AND INDUCED REACTIONS

Catalyzed reactions and induced reactions always involve an increase of the reaction velocity of reactions without any change of the position of the equilibrium. The analytical importance of these reactions, whose velocity can be altered, resides in the fact that even exceedingly minute quantities of materials can be detected through the agency of the accelerated reaction. Furthermore, these effects frequently are due solely to certain materials; in other words, the effects are specific or selective.

In principle, every establishment of differences in the reaction rates of a normal and of a catalytically accelerated reaction is a possible basis for the recognition of the presence of a catalyst. For practical purposes, the only catalyzed reactions that need be considered are those in which the rate is so greatly increased that the acceleration can be detected without applying extremely delicate procedures. The presence of a particular catalyst may then be established by testing for a reaction product, either with or without making a comparative test, depending on the velocity of the catalyzed and the uncatalyzed reaction.

A fundamentally different mode of employing catalysis utilizes a reaction of the material to be detected that has no analytical value merely because normally it proceeds too slowly. Such a reaction can be

accelerated to the point where the detection becomes feasible provided a suitable catalyst can be found. The catalyzed reaction then does not serve to detect the catalyst, but the catalyst aids in increasing the sensitivity of a test.

A complete understanding of the mechanism of catalyzed and induced reactions is not yet available. However, they can be classified, to a certain extent, into different groups with supposedly similar mechanisms. This division is used here.

It has been repeatedly emphasized in the foregoing discussion that frequently complex formation can be regarded as the cause of catalytic action. The interesting behavior of HCl in the presence of AgCl discovered by Lang,[47] may be taken as an example of this complex catalysis. Whereas dilute hydrochloric acid reacts very slowly with manganese dioxide, or manganic or ceric salts, the reduction of these compounds proceeds very rapidly in the presence of even extremely small quantities of a silver salt. Feigl worked out a sensitive test for silver[48] on the basis of this finding. Bobtelsky and his coworkers[49] found that hydrochloric acid reacts much faster also with chromate and vanadate if silver chloride is present. This activation probably is connected with the ability of silver chloride to combine with hydrochloric acid to form $H[AgCl_2]$, whereby the coordinated hydrochloric acid molecule develops a stronger reducing action. Since chlorine, the end product of the reaction, has no action on silver chloride, even small quantities of the latter, can act as a permanent catalyst since they are not consumed.[50]

The activation of chlorate solutions by osmium tetroxide[51] is a further example of complex catalysis. Alkali chlorates in neutral or slightly acid solution have only a low oxidizing power, but in the presence of OsO_4 the chlorate oxygen is transferred, with simultaneous formation of chloride,

[47] R. Lang, Z. anorg. allgem. Chem. **152**, 197 (1926); Ber. **60**, 1389 (1927).

[48] F. Feigl and E. Fränkel, Ber. **65**, 544 (1932).

[49] M. Bobtelsky, Z. anorg. allgem. Chem. **189**, 196 (1930); M. Bobtelsky and S. Czosnek, ibid. **205**, 401 (1932); M. Bobtelsky and L. Chajkin, ibid. **209**, 95 (1932).

[50] Possibly the tendency to form soluble $H[AgCl_2]$ leads, as a preliminary stage, to the adsorption of HCl on the surface of particles of AgCl. In this adsorbed condition, the HCl might not behave as dissociated hydrochloric acid (see p. 523), and accordingly react more rapidly than dilute HCl with MnO_2, ceric salts, chromic acid, etc. If this postulate is valid, the activation of HCl by AgCl would be a case of heterogeneous catalysis (compare p. 138). The idea of heterogeneous catalysis is supported by the fact that not only AgCl but also AgBr, AgI, and AgCN bring about activation of hydrochloric acid toward Mn^{VII}, Ce^{IV}, and Cr^{VI} [compare F. Feigl, J. Chem. Education **20**, 241 (1943)]. Lead chloride, which likewise is able to add HCl, accelerates, in both solid and dissolved condition, these redox reactions of hydrochloric acid.

[51] K. Hofmann, Ber. **45**, 3329 (1912).

to numerous oxidizable inorganic and organic compounds. This enhancement of the reactivity of chlorates probably is connected with the formation of a soluble compound of chlorate and osmium tetroxide. Hofmann, Ehrhart and Schneider[52] showed that the solubility of potassium chlorate is greater in neutral solutions of osmium tetroxide, and also that the oxidation potential of $KClO_3$—OsO_4 mixture is abnormally high. A test for minimal quantities of osmium is made possible through the activation of chlorates by osmium tetroxide.[53] Gleu[54] found that OsO_4 can catalyze other oxidation reactions. Of course, these cases involve a different mechanism than that of the activation of chlorate. For example, the reaction, in sulfuric acid solution, between arsenious acid and bromic acid, hydrogen peroxide, manganese dioxide, ceric salts, and permanganate, are accelerated strongly. The same holds for the reaction between arsenite and ferricyanide, which proceeds but slowly in alkaline solution. The catalysis by OsO_4 can be used in the titrimetric determination of As_2O_3 by $KMnO_4$ or ceric salts in the presence of sulfuric acid.

The increase of the reactivity, in the foregoing examples, can be ascribed to the formation of a complex compound. However, the production of principal valence compounds can also lead to an increased reactivity. Thus, hydrogen peroxide normally reacts with sodium thiosulfate, in acetic acid solution, to form sodium tetrathionate, but in the presence of molybdate the reaction leads to sulfate because of the intermediary formation of permolybdic acid.[55] Feigl[56] found that this same alteration of the course of this reaction can be accomplished with other peracid-formers, such as tungstates, vanadates, zirconium, thorium, and titanium salts (see p. 125) and, according to Komarowsky and Schapiro,[57] with niobium and tantalum. The formation of sulfate in these instances actually involves a new course of reaction, and not merely an oxidation of tetrathionate to sulfate by some per salt that may have been formed. Consequently it is remarkable that hydrogen peroxide and iron salts, which singly do not affect tetrathionate, lead to an oxidation to sulfate if they are present together.[58] Other polythionates (with the exception of dithionate) likewise are oxidized to sulfate by hydrogen peroxide in acetic acid solution, if small quantities of iron salts are added. This catalyzed formation of sulfate can be used

[52] K. HOFMANN, O. EHRHART and O. SCHNEIDER, *Ber.* **46,** 1658 (1913).
[53] F. FEIGL, Spot Tests, p. 107.
[54] K. GLEU, *Z. anal. Chem.* **95,** 306 (1933).
[55] E. ABEL, *Monatsh.* **34,** 821 (1913); *Z. Elektrochem.* **19,** 480 (1913).
[56] F. FEIGL, *Z. angew. Chem.* **44,** 741 (1931).
[57] A. KOMAROWSKY and M. SCHAPIRO, *Mikrochim. Acta* **3,** 144 (1938).
[58] F. FEIGL, *Z. angew. Chem.* **44,** 741 (1931).

to detect easily quantities of iron salts that are so minute that they can give not more than a barely perceptible thiocyanate reaction.

A catalysis of the oxidizing action of hydrogen peroxide has been observed also in its reaction with bromides, and with arsenious acid in acid solution.[59] The former reaction, which leads to the liberation of bromine, is accelerated strongly by peracid-formers as well as by iron salts; the latter reaction, whose product is arsenic acid, is hastened especially by tungstate and molybdate. Intermediate formation of peracids is involved, except in the case of iron. The catalytic activity with salts of zirconium, thorium, titanium, and iron can be prevented by the addition of fluorides, because the active ions practically disappear as a result of the formation of soluble complex fluorides.

The activation of hydrogen peroxide by peroxyacid-formers is closely connected with the finding by Brode[60] that molybdic and tungstic acid catalytically speed up the reaction: ·

$$H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2$$
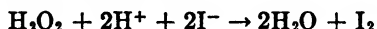
If molybdate or tungstate are absent, this reaction, in strongly acidified solutions, proceeds at an extremely low rate, particularly when only small amounts of hydrogen peroxide are present. Kolthoff[61] utilized the catalyzability of this reaction in the iodometric determination of peroxides.

In the foregoing examples of "intermediate reaction catalysis" there is first a reaction between the catalyst (*cat*) and one reactant (*A*). The product undergoes reaction with the second reactant (*B*), with regeneration of the catalyst. Intermediate reaction catalysis can be represented by the general scheme:

A + B = AB	˙ I (uncatalyzed reaction) (slow)
. A + cat = A·cat	II (primary reaction) (rapid)
A·cat + B = AB + cat	III (secondary reaction) (rapid)

A + B = ˙AB	II + III (catalytically accelerated reaction)
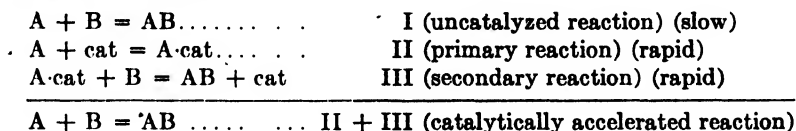
In this scheme, *A·cat* is not necessarily a compound of the catalyst with one of the reactants; it may be, for instance, a reduction product of the catalyst which, by means of III, may be reoxidized to the original combining form of the catalyst. This reaction scheme also shows that it is not strictly correct to say that a catalyst accelerates a reaction. Rather, it is a reaction of the catalyst that speeds up a reaction which *per se* proceeds slowly. Nevertheless, it is customary to speak of "catalysts," and not, as would be more appropriate, of "catalyzing reactions."

An illuminating example of an intermediate reaction catalysis is

[59] F. DEUTSCH, Dissertation, Vienna, 1934.

[60] J. BRODE, *Z. physik. Chem.* **37**, 257 (1901).

[61] I. M. KOLTHOFF, *Z. anal. Chem.* **60**, 400 (1921).

furnished by sodium azide and iodine. They normally react at an extremely low rate, but the reaction occurs instantaneously if sodium thiosulfate or sodium sulfide is added. This was first observed by Raschig.[62] He has suggested the following mechanism for the $Na_2S_2O_3$—I_2 reaction and the catalytic action of sodium thiosulfate. The thiosulfate does not react directly with iodine. Sodium iodothiosulfate is formed first, as shown by (I). This labile compound reacts in turn with an additional molecule of sodium thiosulfate to produce tetrathionate (II). The summation of (I) and (II) gives (III), the usual equation for the oxidation of thiosulfate by iodine to tetrathionate:

$$Na_2S_2O_3 + I_2 = NaIS_2O_3 + NaI \dots \qquad \dots (I)$$
$$NaIS_2O_3 + Na_2S_2O_3 = NaI + Na_2S_4O_6 \qquad \dots (II)$$
$$\overline{2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6 \dots \dots \dots (III) = (I) + (II)}$$
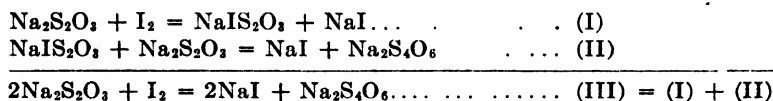
If sodium thiosulfate is added to a solution of sodium azide and iodine, sodium iodothiosulfate is formed first (IV), and this labile compound then reacts with sodium azide (V) rather than with thiosulfate (II). Summation of (IV) and (V) gives (VI), which represents the catalyzed azide-iodine reaction, in which the catalyst ($Na_2S_2O_3$) does not appear:

$$Na_2S_2O_3 + I_2 = NaI + NaIS_2O_3 \dots \dots \qquad \dots (IV)$$
$$NaIS_2O_3 + 2NaN_3 = NaI + Na_2S_2O_3 + 3N_2 \qquad \dots \dots (V)$$
$$\overline{2NaN_3 + I_2 = 2NaI + 3N_2 \qquad \dots \dots (VI)}$$
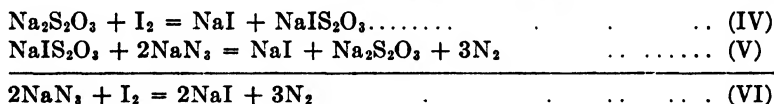
An analogous reaction mechanism, with production of the labile intermediate compound ISNa, can be assumed when explaining the catalytic activity of sodium sulfide on the iodine-azide reaction. Feigl[63] has shown that the catalysis of the iodine-azide reaction, which proceeds with consumption of iodine and evolution of nitrogen, is brought about by even minute quantities of thiosulfate or sulfide, and sensitive tests for these materials were developed on the basis of this catalytic effect. From the practical standpoint, it is particularly significant that even insoluble metal sulfides[64] such as CuS, HgS, As_2S_3, etc., and also organic

[62] F. Raschig, *Ber.* **48**, 2088 (1915). See also his Schwefel und Stickstoff Studien, p. 201. Berlin, 1924.

[63] F. Feigl, *Z. anal. Chem.* **74**, 369 (1928).

[64] Conforming to Raschig's concepts, the following mechanism can be applied to the sulfides of polyvalent metals:

$$MeS + I_2 \rightarrow IMe(SI) \dots \dots \dots \qquad \dots (I)$$
$$IMe(SI) + 2NaN_3 \rightarrow MeS + 2NaI + 3N_2 \quad \dots \dots (II)$$
$$\overline{2NaN_3 + I_2 \rightarrow 2NaI + 3N_2 \dots \dots \quad \dots \dots (III) = (I) + (II)}$$
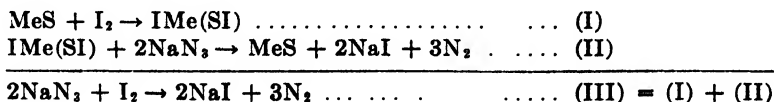
The compound IMe(SI) can be regarded as the isomer of $MeS \cdot I_2$, *i.e.*, as an addition compound of iodine on the metal sulfide. The existence of such addition compounds

compounds containing C=S and C—SH groups react immediately with iodine-sodium azide solution (see p. 146). Since free sulfur or selenium and tellurium compounds, as well as compounds of sexivalent sulfur, exert no influence on the iodine-azide reaction, a series of selective and sensitive tests can be based on the catalyzed acceleration of this reaction.

An example of a rather different kind of catalytic action is the acceleration of the reaction

$$H_2O_2 + 2S_2O_3^{--} + 2H^+ = 2H_2O + S_4O_6^{--}$$

by iodide ion.[65] Hypoiodite ion is formed:

$$H_2O_2 + I^- = H_2O + IO^-$$

and it then reacts with $S_2O_3^{--}$ to regenerate the catalyzing iodide ion:

$$IO^- + 2S_2O_3^{--} + 2H^+ = S_4O_6^{--} + I^- + H_2O$$
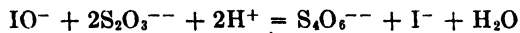
An analogous reaction mechanism is the basis of the iodide ion catalysis of the decomposition of hydrogen peroxide. The hypoiodite formed initially reacts with peroxide to liberate oxygen and regenerate the catalyst:

$$IO^- + H_2O_2 = H_2O + O_2 + I^-$$
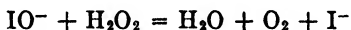
Rupp[66] recommended this iodide ion catalysis for the rapid decomposition of hydrogen peroxide in alkaline solution.

Further examples of intermediate reaction catalysis due to iodide ion can be cited. Lang,[67] in a study that is a model example of the application of catalyzed reactions in quantitative analysis, showed that the reaction:

$$5As_2O_3 + 4MnO_4^- + 12H^+ = 5As_2O_5 + 4Mn^{++} + 6H_2O$$
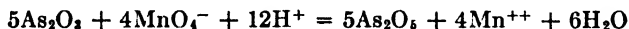
which, of itself, proceeds slowly in acid solution and which, because of

is quite likely, since metal sulfides can be converted into the corresponding iodides by the action of free iodine. The addition compound may well function as the preliminary stage in this conversion. Possibly the isomers are in equilibrium and this condition is constantly upset by reaction (II). This assumption would plausibly explain the catalytic hastening of the iodine-azide reaction by insoluble sulfides. The reactive intermediate compounds given in the foregoing equations are hypothetical. This means, that while their postulation satisfactorily explains the mechanism of the catalysis, their actual existence has not been proved, since the compounds have not been isolated. This failure is not surprising because the lability and reactivity of the intermediate compounds of a catalyst are the very characteristics responsible for the catalytic effect.

[65] E. Abel, *Monatsh.* **41**, 405 (1920).

[66] E. Rupp, *Ber. pharm. Ges.* **44**, 57 (1934).

[67] R. Lang, *Z. anorg. allgem. Chem.* **152**, 197 (1926); see also *Z. anal. Chem.* **85** 170 (1931).

the production of manganic salt does not correspond exactly to the equation given, proceeds rapidly and stoichiometrically in the presence of minute quantities of iodide. The efficacy of the iodide ion is due to its instantaneous reaction with the manganic salt to product manganous salt and iodine. The latter reacts with As_2O_3 and regenerates iodide ion:

$$As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4H^+ + 4I^-$$
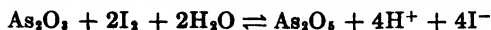
This intermediate reaction catalysis makes it possible to standardize accurately either arsenite or permanganate solutions. Willard[68] found that small quantities of iodide accelerate the reaction of ceric salts with arsenite, oxalate, and other oxidizable compounds to such an extent that standard solutions of ceric salts can be used in oxidimetry.

The fact that certain oxidations by persulfate ions can be accelerated by silver ions was first observed by Marshall.[69] This effect is likewise the result of an intermediate reaction catalysis. The activity of the silver is displayed even in the autodecomposition of acidified solutions of alkali persulfates. Whereas silver-free solutions are subject to a gradual decomposition: $H_2S_2O_8 + H_2O \rightarrow 2H_2SO_4 + O$, which becomes complete only on evaporation, the reaction occurs rapidly if Ag^+ ions are present. This can be demonstrated easily if a little methyl orange is put into the solution. The color is discharged far more quickly in the silver-bearing solutions. The indicator is broken down into colorless products by the atomic oxygen. The action of the silver probably involves the production of labile, and therefore very reactive, Ag^{II} compounds.[70] They accomplish the oxidation, Ag^I is regenerated, is again converted to reactive Ag^{II} by persulfate, and so on. Possibly the persulfate of divalent silver is involved in this cycle. In the absence of oxidizable materials, Ag^{II} may well react with excess persulfate ions; mutual reduction ensues, and atomic oxygen is produced. When oxidizable materials are available, they are oxidized by the atomic oxygen or by Ag^{II}. Consequently, acidified, silver-containing persulfate solutions can accomplish oxidations which are not brought about by persulfate alone, or more correctly, only at an immeasurably slow rate. Sensitive tests for manganese and chromium are based on the fact that persulfate in the presence of silver salts smoothly oxidizes acid solutions of Mn^{++} and Cr^{+++} ions to permanganate and chromate, respectively.[71] A widely used colorimetric

[68] H. Willard and P. Young, *J. Am. Chem. Soc.* **50**, 1322, 1372 (1928).

[69] H. Marshall, *Proc. Roy. Soc. Edinburgh* **23**, 163 (1900).

[70] Compare A. Travers, *Compt. rend.* **182**, 972 (1926); A. Pinkus and L. Ramakers, *Bull. soc. chim. Belges.* **41**, 529 (1932).

[71] H. Marshall, *Chem. News* **83**, 76 (1901); *Z. anal. Chem.* **43**, 418 (1904); F. Ibbotson and R. Howden, *Chem. News* **90**, 320 (1904). Application of these tests for manganese and chromium in spot test analysis are described in F. Feigl, Spot Tests, pp. 129 and 132.

procedure for manganese makes use of this catalyzed oxidation to permanganate. Persulfate has practically no effect on warm solutions of oxalic acid containing sulfuric acid, but the reduction of the persulfate proceeds quantitatively in the presence of a few milligrams of silver sulfate.[72] A reliable method for determining active oxygen in persulfate was based in this finding. The effect of silver ions on the redox reaction between arsenious acid and persulfate, in the presence of nitric acid, is quite impressive, if the reaction is carried out with zirconium nitrate also present. Whereas the silver-free mixture remains clear for many hours, acid-insoluble zirconium arsenate gradually deposits when silver is present.[73]

A very nice application of an oxidation by persulfate that is catalyzed by silver salts was discovered by Oberhauser and his associates.[73a] They found that when organic compounds are heated with potassium persulfate, silver sulfate and sulfuric acid, under readily obtainable conditions, the samples are quantitatively decomposed with formation of carbon dioxide. This result makes it possible to determine carbon in organic compounds in a wet way. Willard and Young[73b] made especially interesting studies of the use of the catalytic hastening of redox reactions of persulfate by silver salts. They not only worked out an elegant solution of a difficult analytical problem but they also provided an insight into the selectivity of catalysis reactions. It had been known for a long time that cerous salts can be oxidized to ceric salts by persulfate in the presence of sulfuric acid. Basic insoluble ceric salts result if insufficient acid is present. If too much acid is present, the oxidation is incomplete or it may not proceed at all. The reason is that strongly acidified persulfate solutions, when heated, not only undergo hydrolysis to produce atomic oxygen (see p. 128), but also permit of the following hydrolysis: $H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$. In other words, hydrogen peroxide is produced, which reduces ceric to cerous salts. Willard and Young showed that, in the presence of silver salts, there is complete and rapid oxidation of cerous salts, even in strong acid solutions, and hence, there is no interference from hydrogen peroxide. Since, as was shown previously, excess persulfate in acid solution is quickly and completely decomposed on warming in the presence of silver salts, the resulting ceric content of the solution can be determined accurately by titration. The findings of Willard and Young show that of the two hydrolytic processes

[72] R. KEMPF, *Ber.* **38**, 3963 (1905).

[73] F. FEIGL, unpublished studies.

[73a] F. OBERHAUSER, B. A. RIVIERA, and H. ETCHEVERRY, *Chem. Abstracts* **41**, 1950 (1947).

[73b] H. H. WILLARD and P. YOUNG, *J. Am. Chem. Soc.* **50**, 1380 (1928).

$$H_2S_2O_8 + H_2O \rightarrow 2H_2SO_4 + O \ldots (I)$$
$$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2 \ldots (II)$$
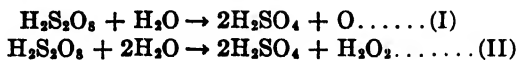
only (I), but not (II), is accelerated by silver salts. If both reactions were catalyzed, there would be no difference in the behavior of strongly acidified solutions of persulfate toward cerous salts in the presence or absence of silver salts. Accordingly, this is a clear instance of a selective action of silver ions, because they catalyze only one of these reaction of the persulfate, and have no effect on the other. In this case the catalyst determines the course of the reaction. Another example of forcing a reaction to take a new path was cited on p. 124, where it was pointed out that the $Na_2S_2O_3$—H_2O_2 reaction, in the presence of the catalytically active peracid-formers, produces sulfate rather than tetrathionate.

A catalytic activity similar to that of the silver ion is also exhibited by other metals that can easily change reversibly from one to another of their several valences. Copper and iron salts, especially, show this. For instance, the reaction between ferric salts and thiosulfate which, if partial reactions are disregarded, proceeds according to the equation:

$$2Fe^{+++} + 2S_2O_3^{--} = 2Fe^{++} + S_4O_6^{--}$$
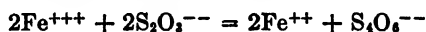
is greatly accelerated by copper salts.[74] A dark red-brown color (ferric thiosulfate) appears first, and this fades as the reduction of the ferric salt proceeds. As little as 0.2γ copper can be detected by the shortening of the time required to discharge the color. It is probable that the cupric ion first oxidizes the thiosulfate to tetrathionate, and the resulting cuprous ion or complex cuprous thiosulfate is reoxidized to cupric ion by the ferric salt. This assumption is supported by the fact that other reduction reactions of sodium thiosulfate are also distinctly catalyzed by copper salts. For instance, the redox reaction

$$V_2O_5 + 2S_2O_3^{--} + 2H^+ = V_2O_4 + S_4O_6^{--} + H_2O$$
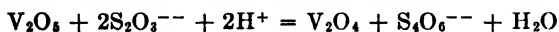
is accelerated by small quantities of copper sulfate.[75] This is true likewise of the reduction by sodium thiosulfate of molybdate, phosphomolybdic acid, and chromate.[76]

Copper salts exert an interesting catalytic action on alkali hypobromites.[77] Even at great dilution, they bring about a decomposition of the latter into bromide with evolution of oxygen.[78] Cobalt and nickel salts (but not Mn, Pb, Bi, etc.) exhibit an action analogous to but

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[74] F. HAHN and G. LEIMBACH, *Ber.* **55**, 3070 (1922).

[75] G. OBERHELMANN, *Am. J. Sci.* [4] **39**, 530 (1915).

[76] F. FEIGL, Unpublished studies; compare also A. STEIGMANN, *Phot. Korr.* **70**, 54 (1935).

[77] P. FLEURY, *Compt. rend.* **171**, 957 (1927).

[78] K. FILIMANOWITSCH, *Chem. Abstracts* **25**, 5640 (1931).

weaker than that of copper salts. This effect, *i.e.*, the production of atomic oxygen, is clearly connected with the observation of Filimanowitsch[78] that hypobromites, which normally oxidize manganous salts to manganese dioxide, produce permanganate.if copper salts are present. This action can be used for the detection of copper or manganese.[79] The oxidation of hypophosphate to phosphate by hypobromite is hastened if small quantities of copper, cobalt, or nickel salts are present.[80] That these metals exert a like qualitative effect on these oxidations argues for the activity of higher metal oxides; the particularly strong catalytic effect of copper possibly can be ascribed to the instability of Cu^{III} oxide. Evidence for this assumption was seen by Feigl and Uzel[81] in their observation that telluric and periodic acids, which can form stable Cu^{III} complexes, destroy the catalytic effect of copper on the reaction between manganous salt and hypobromite. This "poisoning" of the catalysis can be used as a very delicate test for these acids.[82] It illustrates the fact that not only a catalytic action, but also the inhibition of a catalytic acceleration may have analytical significance and value. The remarkable discovery that copper salts can catalytically accelerate reductions as well as oxidations is clearly to be explained on the basis that, by alternation of valence and regeneration of Cu^{II} salt, unstable strongly reducing Cu^{I} salts and unstable strongly oxidizing Cu^{III} salts can be produced.

Iron salts also act as catalysts for numerous oxidations; they react with the substrate and are reduced to ferrous salts. The latter are rapidly reoxidized by the oxidizing agent, hydrogen peroxide, for example. The oxidation reactions that are accelerated by ferrous but not by ferric salts are remarkable. In the presence of ferrous salts hydrogen peroxide is a much stronger oxidizing agent than usual. For instance, tartaric acid, which does not react with hydrogen peroxide by itself, is oxidized to dihydroxymaleic acid if small amounts of ferrous or copper salts are introduced.[83] Tartaric acid in acid solution is completely and easily destroyed by warming with hydrogen peroxide (6%) plus iron or copper salts.[84] This effect can be used to liberate Al^{+++} ions from complex aluminum-tartrate solutions (compare p. 108).

Numerous cases are known in which the velocity of a given reaction is increased because another apparently indifferent reaction occurs simul-

[79] F. Feigl and E. Fränkel, *Ber.* **65**, 541 (1932).

[80] B. Blaser and P. Halpern, *Z. anorg. allgem. Chem.* **215**, 33 (1933).

[81] F. Feigl and R. Uzel, *Mikrochemie* **19**, 134 (1936).

[82] F. Feigl. Spot Tests, pp. 225, 267.

[83] H. Fenton and H. Jones, *Proc. Chem. Soc.* (*London*) **15**, 244 (1899); see also *J. Chem. Soc.* **87**, 804 (1905).

[84] W. Meigen and J. Schnerb, *Z. angew. Chem.* **37**, 208 (1924).

taneously or immediately beforehand.   Kessler (1863) coined the term *induced reactions* for these remarkable effects.[85]

A classic example of such reactions, which in homogeneous solutions usually concern oxidation processes, is the behavior of bromic acid toward As_2O_3 in the presence of sulfur dioxide.   The oxidation to As_2O_5 ordinarily proceeds quite slowly, but it starts instantly if the oxidation of SO_2 by $HBrO_3$ occurs along with it.   The reaction:

$$3SO_3^{--} + BrO_3^- = 3SO_4^{--} + Br^-$$
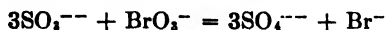
is called the *inducing reaction;* the reaction:

$$3As_2O_3 + 2HBrO_3 = 3As_2O_5 + 2HBr$$
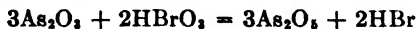
the *induced reaction.*   It is characteristic of such coupled reactions that they always have a common reaction component, termed the *actor.* The material that by reaction with the actor causes the reaction to occur is termed the *inductor*, and the substance which thereby is caused to undergo chemical change is called the *acceptor.*   In the present example, $HBrO_3$ is the actor, SO_2 the inductor, As_2O_3 the acceptor.   The ratio between the quantities of the actor consumed by the acceptor and by the inductor is called the *induction factor.*   In true coupled reactions this is a rational number.   The induction factor of purely catalytic processes is practically infinite.   There are numerous transitions between the coupled reactions that are characterized by stoichiometric relationships and real catalyses.   The rule discovered by Skrabal is of great importance.   It states that the extent of the induced reaction is greater, the more slowly the inducing reaction proceeds.   The consequence is that an extraordinarily great inductive action is frequently accomplished by amounts of a material so small that they could react but slowly if the law of mass action alone were operative.

In general, the inducing reaction that proceeds at a higher rate can be distinguished from the induced reaction which *per se* has a lower or, in some cases, an immeasurably small reaction velocity.   It is then possible to state which of the reactants is functioning as actor, inductor, or acceptor.   According to the Skrabal rule even slow inducing reactions can exert considerable induction effects.   Consequently, it may be expected that coupled reactions will be encountered in which, lacking knowledge of the respective reaction rates, it will not be possible to decide which of two concurrent reactions induces the other.   The system:

[85] See the excellent monograph by A. SKRABAL, Die Induzierten Reaktionen, ihre Geschichte und Theorie; Stuttgart, 1908.   See also W. FRANKENBERGER and F. DÜRR, Katalyse (Enzyklopädie der techn. Chemie, Vol. 6).   Vienna, 1930; I. M. KOLTHOFF and V. A. STENGER, Volumetric Analysis, Vol. 1, p. 168.   New York, 1942; I. M. KOLTHOFF and R. LIVINGSTON, *Ind. Eng. Chem., Anal. Ed.* **7**, 209 (1935).

indigo–oxalic acid–bichromate is a pertinent instance. The $K_2Cr_2O_7$ is doubtless the actor, since it oxidizes the oxalic acid as well as the indigo, which it decolorizes. However, if certain concentrations and pH values are maintained, both oxidations are very. slow. Accordingly, stable solutions of oxalic acid plus bichromate, and indigo plus bichromate, can be prepared. If such solutions are put together reaction occurs at once, as evidenced by the disappearance of the indigo color. The rapid oxidation of indigo by chromate in the presence of oxalic acid is the basis of a process that has been used for a long time in cotton dyeing. This discharging process, which is applied to indigo and other vat dyes, was probably discovered empirically or by accident. Georgievics and Springer[86] made a scientific study of this coupled reaction. They found that the rate at which the indigo color is discharged is proportional to the concentration of the oxalic acid, provided all other conditions are constant.[87] Consequently, the oxalic acid-bichromate reaction seems to be the inducing reaction. The coupled oxalic acid–indigo–bichromate oxidation has been used to detect oxalic acid;[88] as little as 30γ oxalic acid in 5 ml. can be recognized through the hastened discharge of the indigo color. Unfortunately, the reaction is not specific for oxalic acid. Georgievics and Springer found that other aliphatic and aromatic carboxylic acids, and likewise alcohol and glycerin, have an analogous though less pronounced action than oxalic acid.[89] Another coupled reaction system, in which the inducing and induced reaction cannot be identified immediately, was described by Tananaeff and Schapowalenko.[90] In this case, alkaline arsenite reacts with a mixture of gold and palladium salts. In the cold, neither of these, if alone, reacts with the arsenite, but in mixtures there is immediate reduction to metallic gold and palladium. This action has been utilized by these workers for detecting arsenite.

The preceding tests have no particular analytical significance because simpler, more decisive, and more sensitive tests are available for oxalic and arsenious acid. However, the present discussion must include a further consideration of the special position occupied by the coupled

[86] G. N. Georgievics and L. Springer, Sitzber. Akad. Wiss. Wien. 109, II, 308 (1900).

[87] Possibly, small quantities of oxalic acid could be determined quantitatively by a chronometric method, if, under fixed conditions, measurements were made of the time required to discharge the color of a standard solution of indigo.

[88] N. A. Tananaeff and A. A. Budkewitsch, Z. anal. Chem. 103, 353 (1935). They seemingly were not cognizant of the work of Georgievics and Springer (loc. cit.) since they credit N. Schilow with the coupled reaction used in this test.

[89] Compare A. S. Komarowsky and W. A. Nasarenko, Z. anal. Chem. 104, 413 (1936).

[90] N. A. Tananaeff and A. M. Schapowalenko, Z. anal. Chem. 100, 352 (1935).

reactions that underlie these tests for oxalic and arsenious acid. They clearly demonstrate that induction effects, stemming from systems whose reactions are innately sluggish, can be utilized to accomplish analytical ends. Little attention has heretofore been given to this possibility. The majority of the induced reactions used up to the present involve inducing reactions in which a relatively large number of materials participate. In addition, the inducing reaction proceeds rapidly, and seemingly an induction action takes place only so long as the inducing reaction is occurring. It should be remembered, however, that there is always a consumption of one of the reactants during the course of an inducing reaction and a concentration range is invariably reached at which, due to this impoverishment, the inducing reaction must slow up. However, an induction effect is possible even at this stage. This was demonstrated in a study of the action of permanganate on a solution containing oxalic acid plus mercuric chloride. Unless irradiated, oxalic acid and mercuric chloride do not act on each other. Oberhauser and his collaborators,[91] and before them Dhar,[92] proved that the reaction between permanganate and oxalic acid, if carried out in a solution containing mercuric chloride, causes immediate precipitation of mercurous chloride. Hence the reaction

$$2HgCl_2 + H_2C_2O_4 \rightarrow Hg_2Cl_2 + 2HCl + 2CO_2$$
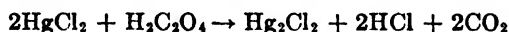
is brought about. In other words, this inherently slow reaction is induced by the comparatively rapid redox reaction between permanganate and oxalic acid. Oberhauser postulated the production of activated oxalic acid.[93] He adduced in support of this assumption the fact that a dilute solution of permanganate, when decolorized by excess oxalic acid, still retains the ability to reduce mercuric chloride; the reducing action of such apparently exhausted permanganate solutions toward mercuric chloride decreases or disappears only after several hours. This time phenomenon would be entirely consistent with an induced reaction if it is also assumed that optically invisible quantities of permanganate remain in these decolorized solutions. This minute residue could then slowly react with oxalic acid, and exert an inducing action during this period.[94] Oberhauser was able to show that mercury

[91] F. OBERHAUSER and W. HENSINGER, Ber. 61, 521 (1928); F. OBERHAUSER and J. SCHORMUELLER, Ann. 470, 111 (1929).

[92] N. DHAR, J. Chem. Soc. 111, 690 (1917).

[93] Compare E. ABEL, Z. Elektrochem. 43, 629 (1937).

[94] This view is supported by the following unpublished observations of F. FEIGL. The quantity of Hg_2Cl_2 precipitated from a solution of HgCl_2 increases the more slowly the KMnO_4-H_2C_2O_4 reaction is carried on (dilution; gradual, drop-wise addition of KMnO_4 and H_2C_2O_4). Furthermore, an inducing effect of KMnO_4-H_2C_2O_4

can be quantitatively precipitated, as mercurous chloride, if the oxalic acid-permanganate reaction takes place in a solution of mercuric chloride. Mercury can thus be separated from bismuth and cadmium. This is the only known instance of a direct gravimetric method based on the employment of an induced reaction.[95]

An interesting induction action is the oxidation of green hydrated nickel[II] oxide in the presence of sulfur dioxide, forming black hydrated nickel[IV] oxide. This was first observed by Wicke[96] and later studied by Haber and Bran.[97] The mechanism of the induced oxidation of $Ni(OH)_2$ probably is that basic nickel sulfite is formed first. This then undergoes autoxidation:

$$Ni—OH \diagdown SO_3 + O_2 + H_2O \rightarrow Ni(OH)_4 + NiSO_4$$
$$Ni—OH \diagup$$
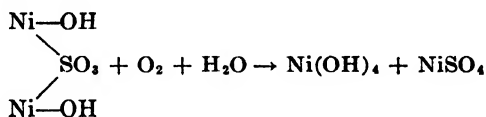
in both its cationic and anionic parts. According to Feigl and Fränkel[98] this effect can be used as a delicate test for sulfite. In this connection it should be noted that sulfurous acid can activate other oxidation reactions. Schönbein[99] observed, long ago, that the slow decolorization of indigo solutions by ferric salts proceeds very rapidly after the addition of sulfite. Later, Schaer[100] found this same action of sulfur dioxide in the oxidation of indigo (in part also of pyrogallol) by chlorate, bromate, and iodate.

A rather remarkable induction occurs during the autoxidation of $Mn(OH)_2$ to MnO_2 in the presence of $Co(OH)_2$. Although pure $Co(OH)_2$ is quite stable when dry, it is extensively oxidized to $Co(OH)_3$ by the air if manganous salts are present (up to a ratio $Mn:Co = 1:200$).[101] The explanation for this oxidation of $Co(OH)_2$ to $Co(OH)_3$ is probably the following. The autoxidation of $Mn(OH)_2$ consumes one-half molecule of

was observed only toward $HgCl_2$, but not toward palladium and platinum salts. The latter would be expected to react, if an active form of oxalic acid really is formed.

[95] F. OBERHAUSER (loc. cit.) states that the quantitative precipitation of 0.1 g. mercury as Hg_2Cl_2 requires the addition of 30 ml. $N/10$ sodium oxalate and 2 ml. $N/10$ $KMnO_4$, and 10 minutes warming in the water bath (70°C.). This prescription strongly indicates that the precipitation of Hg_2Cl_2 takes place not only during, but also after, the reduction of the permanganate. A visible disappearance of the permanganate color requires less than one minute.

[96] C. WICKE, Z. f. Chem. 8, 89, 305 (1865).

[97] F. HABER and F. BRAN, Z. physik. Chem. 35, 81, 608 (1900); compare also W. BÖTTGER and E. THOMÄ, J. prakt. Chem. 147, 11 (1936).

[98] F. FEIGL and E. FRÄNKEL, Ber. 65, 545 (1932).

[99] C. SCHÖNBEIN, J. prakt. Chem. [1] 89, 5 (1863).

[100] E. SCHAER, Ann. 323, 32 (1902).

[101] Private communication from L. MELNIK, Ghent.

oxygen per each molecule of $Mn(OH)_2$: $Mn(OH)_2 + \frac{1}{2}O_2 \rightarrow MnO(OH)_2$. The other half, *i.e.*, atomic oxygen is taken up by a second molecule of $Mn(OH)_2$. If the $Mn(OH)_2$ happens to be intimately mixed with $Co(OH)_2$, part of the activated (atomic) oxygen produced by the autoxidation of $Mn(OH)_2$ can be consumed by the $Co(OH)_2$ to produce $Co(OH)_3$. Accordingly, in such mixtures, the autoxidation of the $Mn(OH)_2$ induces the autoxidation of the $Co(OH)_2$ which, when alone, is only slightly susceptible to autoxidation. In this connection, it should be pointed out that the autoxidation of $Mn(OH)_2$, or the analogous autoxidation of $Ce(OH)_3$ to $CeO(OH)_2$, is involved in the sensitive spot tests for manganese and cerium. In these,[102] the resulting hydrated oxides of Mn^{IV} or Ce^{IV} act directly on benzidine. The latter also becomes involved in the autoxidation and takes up atomic oxygen. Both of these processes result in the oxidation of benzidine to benzidine blue. This matter is discussed in more detail on p. 332.

Numerous induced reactions are known among reduction processes. It is to be noted that many reduction reactions, that are appropriate *per se*, cannot be translated into quantitative methods of separation. Thus Wöhler and Spengel[103] found that reducing agents which act on platinum salts but not on tin salts are not suitable for separating these metals, because the platinum precipitate always contains tin. Such induced reductions appear to be quite frequent among the noble metals in general.[104] For instance, platinum salts, which are not reduced by hypophosphorous acid,[105] are reduced immediately by it to platinum, quantitatively in fact in weak acid solution, in the presence of palladium salts. The latter react instantaneously with this reducing agent to precipitate metallic palladium.

Induced reductions can often be used to advantage in qualitative analysis. Thus, an induced reaction is the reason for an increased sensitivity that can be secured by carrying out the familiar Vanino-Treubert test for bismuth[106] in the presence of a lead salt. Bismuth hydroxide reacts with alkaline stannite solution to form metallic bismuth and stannate:

$$2Bi(OH)_3 + 3Sn(ONa)_2 = 2Bi^\circ + 3SnO(ONa)_2 + 3H_2O$$
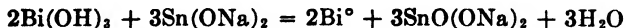
Lead salts react analogously:

$$Pb(OH)_2 + Sn(ONa)_2 = Pb^\circ + SnO(ONa)_2 + H_2O$$
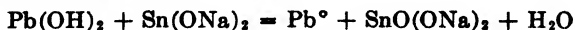
[102] F. FEIGL, *Oesterr. Chem. Ztg.* **22**, 124 (1919); *Chem. Ztg.* **44**, 689 (1920).

[103] L. WÖHLER and H. SPENGEL, *Z. anal. Chem.* **50**, 165 (1911).

[104] L. HOFFMANN and G. KRÜSS, *Ann.* **238**, 66 (1887); L. MOSER and H. HACKHOFER, *Monatsh.* **59**, 486 (1932). Compare F. MYLIUS and A. MAZZUCCHELLI, *Z. anorg. allgem. Chem.* **89**, 1 (1914).

[105] L. MOSER and M. NIESSNER, *Z. anal. Chem.* **63**, 240 (1923).

[106] L. VANINO and F. TREUBERT, *Ber.* **31**, 1113 (1898).

but only after long standing or when warmed. If, however, lead salts are present along with the bismuth salts, the reduction of the lead salts to metallic lead will be accelerated or induced[107] by the reduction to metallic bismuth. This can be accomplished with very small quantities of bismuth salts which, of themselves, give no apparent reaction with stannite, even after long standing. Since, under easily controlled conditions, lead salts when alone do not react, the induced lead reaction can serve as an excellent method for detecting bismuth. The sensitivity of the Vanino-Treubert test can thus be increased 250-fold. The author, in explaining the induced reduction of lead by the reduction of bismuth, assumed originally that bismuth nuclei are involved, and that they serve as crystallization centers for the precipitation of metallic lead. It now seems more probable that an intermediate reaction catalysis occurs, in which the reduction of Bi^{+++} ions to metallic bismuth does not proceed directly. Lower oxides, such as Bi_2O, are formed as intermediate products: $Bi^{III} \rightarrow Bi^{I} \rightarrow Bi^{\circ}$. The univalent bismuth reacts with lead ions: $Pb^{II} + Bi^{I} \rightarrow Bi^{III} + Pb^{\circ}$. Thus Bi^{III} is regenerated, is again reduced by stannite to Bi^{I}, which again can act on Pb^{II}, and so on.

Experiments have confirmed the expectation that the bismuth reduction would be capable of influencing other reductions accomplished with stannite. Thus the stannite reduction of antimony[III], thallium[I], and copper salts is accelerated if bismuth salts are added. To some extent the latter act as sensitizers. Quantities of bismuth, too small to be revealed by the stannite reaction, suffice to accelerate the reduction of antimony and thallium salts.[108] The reduction of cadmium salts by stannite solution, which otherwise does not occur, proceeds smoothly in hot solutions in the presence of small quantities of bismuth.[109] The reaction between silver salts and ferrous salts (also other reducing agents) is accelerated catalytically by the slightest traces of gold salts. Krumholz and Watzek[110] showed that the acceleration could still be detected definitely in 2 ml. of a gold solution diluted $1:5 \times 10^{12}$. This is the most sensitive known case of this kind of reaction. Its mechanism probably is similar to that of the reaction induced by bismuth between lead salts and stannites.

An induced reduction probably also occurs in the action of phenylhydrazine acetate on mercuric chloride solution, in the presence of silver nitrate.[111] Phenylhydrazine reduces $HgCl_2$ to Hg_2Cl_2, and then slowly,

[107] F. FEIGL and P. KRUMHOLZ, *Ber.* **62**, 1138 (1929).
[108] F. FEIGL, unpublished studies.
[109] F. FEIGL, unpublished studies with F. DEUTSCH.
[110] P. KRUMHOLZ and H. WATZEK, *Mikrochim. Acta* **2**, 80 (1937).
[111] F. FEIGL, *Z. angew. Chem.* **44**, 741 (1931).

in part, to mercury.   However, on the addition of traces of silver nitrate, the mercuric chloride solution turns black immediately, due to the production of finely divided mercury.   The concurrent reduction of silver salts by sodium hypophosphite causes an analogous acceleration of the reduction of mercuric chloride and leads, in buffered solution, to calomel.[112]   The separation of calomel is so hastened by even traces of silver salt that this effect forms the basis of a delicate test for silver.   Besides such accelerations of the reduction of mercury salts in the presence of silver salts, mercuric salts themselves can also expedite reductions.   This was shown by King and Brown[113] in the Bettendorf arsenic test.   The reduction of arsenic compounds by stannous chloride in acid solution, on which this test is based,[114] is hastened by mercury salts.   The necessary quantities are so slight that they are not precipitable by stannous chloride.   Consequently a delicate method of detecting mercury was developed.

An observation connected with the foregoing phenomenon was made much earlier by Fresenius,[115] who found that the precipitation of free antimony by zinc is much more rapid if tin is deposited simultaneously. Ordinarily this test is carried out by placing the test solution, along with a particle of zinc, on a piece of platinum foil.   The presence of antimony is then revealed by a gray deposit on the platinum.   If, however, the antimony solution contains a tin salt, this is also reduced, and the metallic tin serves as a crystallization center for the antimony deposit. Smaller quantities of antimony can then be detected than when the solution contains no tin.

The reduction of stannic salts by hypophosphorous acid is hastened if mercuric salts are present.   The latter are reduced very rapidly by this reagent through calomel to free mercury, and this process catalytically speeds up the slow reduction of quadrivalent to divalent tin.   This effect, discovered by Evans,[116] can be used to detect small quantities of mercury.[117]

The catalytic reactions described in the foregoing discussion were examples of homogeneous catalysis, i.e., the catalyst and the reaction components are in the same phase.   In heterogeneous catalysis they are in different phases.   Solid catalysts can be active in reactions between: (a) gases; (b) gases and dissolved materials; (c) gases and

[112] F. HAHN, Ber. 65, 840 (1932).
[113] W. KING and F. BROWN, Ind. Eng. Chem., Anal. Ed. 5, 268 (1933); J. Am. Chem. Soc. 61, 968 (1939).
[114] A. BETTENDORF, Z. anal. Chem. 9, 105 (1870).
[115] R. FRESENIUS, Z. anal. Chem. 1, 444 (1862).
[116] B. EVANS, Analyst 56, 177 (1931).
[117] F. FEIGL and L. BADIAN, unpublished studies; F. FEIGL, Spot Tests, p. 53.

solids; (d) dissolved materials. Instances can be cited from any of the four categories to show that heterogeneous catalysis can be utilized to secure sensitive and selective tests.

J. Doebereiner, in 1823, discovered that relatively large volumes of gases can be taken up at room temperature by platinum metals, and that this adsorption or absorption (see Chapter X) sometimes leads to catalytic effects. For instance, hydrogen taken up by finely divided platinum metals can combine with the oxygen of the air to form water, and the heat of reaction can cause the metal to glow. Curtmann and Rothberg[118] were the first to employ this effect for the detection of these metals. They soaked thin asbestos paper with 0.2 ml. of the salt solution, and by evaporation and ignition deposited the finely divided metal on the paper. While still warm, the paper was held in a mixture of illuminating gas and air. The presence of platinum metals was revealed by a glowing of the asbestos paper. Some years later, Hahn[119] used hydrogen in this glow reaction, and by this and other modifications refined the method so that it could be used in spot test analysis. As little as 0.01γ palladium can be detected by this procedure; the corresponding tests for other platinum metals have sensitivities of the same order of excellence. Only osmium and ruthenium cannot be revealed by the glow reaction as their oxides are too volatile. As early as 1868, Graham[120] showed that hydrogen behaves as though it were nascent (atomic) when it is taken up by platinum metals. This signifies that the gas is then able to reduce mercuric and ferric chlorides, or to convert free halogens to the corresponding halide ions, or to reduce ions of metals more noble than hydrogen to the metal. Such activation of molecular hydrogen by metallic platinum must be brought into relationship with the equilibrium: $H_2° \rightleftharpoons 2H°$, whose position and establishment determines the reducing action of hydrogen. This equilibrium lies far toward the side of molecular hydrogen, and if the atomic hydrogen is consumed in a redox reaction the equilibrium is only slowly reestablished. Consequently, molecular hydrogen is a weak reducing agent; in fact, it acts with extreme slowness. The activation by platinum metals is due to the rapid reestablishment of the foregoing equilibrium when the gas is in contact with these metals. This means that both the production of hydrogen atoms from molecular hydrogen and the reverse process, namely, the recombination of the atoms to form hydrogen molecules, occur rapidly on platinum. Accordingly, the activation of hydrogen on platinum metals is a catalytic process through which the hydrogen atoms removed from the equilibrium

[118] L. P. CURTMANN and P. ROTHBERG, *J. Am. Chem. Soc.* **33**, 708 (1911).

[119] F. L. HAHN, *Mikrochemie* **8**, 77 (1930).

[120] T. GRAHAM, *Proc. Roy. Soc.* (*London*) **16**, 422 (1868).

are resupplied at a high rate.   Zenghelis[121] used this effect in his test for hydrogen.   He showed that no reduction to Mo^V (molybdenum blue) occurs when hydrogen is passed into a warm, slightly acidified, solution of alkali molybdate.   On the other hand, molybdenum blue is produced quickly if the hydrogen is introduced into the molybdate solution in contact with platinum or palladium.   As little as 10γ hydrogen can be detected in this way.[122]

Zenghelis (loc. cit.) reported that the reduction of acidified molybdate solutions to produce molybdenum blue is accelerated also by carbon monoxide if this gas is in contact with platinum or palladium.   In the absence of these metals, there is no visible bluing, even though the gas is passed through the molybdate solution for twenty minutes.   It can be assumed that the reason for this catalytic action is that the gas adsorbed on the platinum or palladium is more reactive than gaseous carbon monoxide.   Perhaps some part is also played by the reaction: $CO + H_2O \rightarrow CO_2 + H_2°$, which Wieland[123] demonstrated as occurring on platinum metals.   The activation of carbon monoxide by palladium and the reduction of sexivalent to quinquevalent molybdenum by the activated gas were used by Feigl and Krumholz[124] as the basis of a very sensitive and specific test for palladium.   The chemistry of this procedure is quite interesting.   Palladium is the only member of this group that is precipitated as the metal by the action of carbon monoxide on acidified solutions of the salts: $Pd^{++} + CO + H_2O \rightarrow Pd° + CO_2 + 2H^+$. If this reaction is carried out in a solution of phosphomolybdic acid, where the molybdenum has been rendered more reactive by complex binding (see p. 115), then the carbon monoxide is activated on the resulting finely divided palladium and can immediately react with the phosphomolybdic acid to produce molybdenum blue.   Consequently, this procedure involves the combination of three effects: (a) the reduction of Pd^{++} ions by carbon monoxide; (b) the activation of carbon monoxide;

[121] C. ZENGHELIS, Z. anal. Chem. **49**, 729 (1910).

[122] The papers by ZENGHELIS and CURTMANN and ROTHBERG contain the first instances of a planned use of catalytic reactions in qualitative inorganic analysis. It is noteworthy, that despite these examples, and in the face of the knowledge of numerous catalytic hastenings, the significance of catalyzed reactions and of the closely associated induced reactions remained almost completely unnoticed for many years with respect to the creation of specific and sensitive tests.   Only after 1928, when the author led the way, did other workers pay any attention to the application of catalytic reactions to microanalytical objectives.   See FEIGL's lecture "Katalyse und Mikrochemie" in Z. angew. Chem. **44**, 739 (1931).   A survey of the literature will confirm the foregoing statement.

[123] H. WIELAND, Ber. **45**, 679 (1912); **54**, 2361 (1921); compare also W. TRAUBE and W. LANGE, Ber. **58**, 2773 (1925).

[124] F. FEIGL and P. KRUMHOLZ, Ber. **63**, 1917 (1930).

(c) the sensitization of molybdenum by complex binding. In this way, it is possible to detect palladium specifically in 1 ml. of solution, even at a dilution of 1 : 40,000,000. Conversely, as little as 1 part of carbon monoxide in 500,000,000 parts of air is revealed by passing the sample over silica gel impregnated with a complex silicomolybdate and palladium sulfate. The color changes from yellow to green; the intensity of the green indicating the degree of contamination of the air by the poisonous gas.[125]

An increase in reactivity, that is often considered as heterogeneous catalysis, is encountered with amalgams, in that the metals combined with mercury frequently exhibit a greater activity than when free. In general, the reducing velocity is increased if the metals are amalgamated. It has been known for a long time that amalgamated aluminum is so sensitive to the moisture of the air that efflorescences (sprouted alumina) form on amalgamated aluminum foil.[126] Schmidt and Tornow[127] used this effect as the basis of a test for mercury and, as modified by Feigl and Badian,[128] it can be carried out also as a spot test. Minimal quantities of mercury (0.001γ Hg) can be detected in this way. The great sensitivity of the test is due to the fact that the mercury itself acts as a catalyst in the reaction. It is temporarily released when the aluminum is converted into the oxide, and then re-forms the amalgam, which again effloresces, and so on.[129]

Reaction accelerations that belong in the realm of heterogeneous catalysis occur, and can be used in certain fuming reactions that can be accomplished with ammonium salts of halogen hydracids. This includes the conversion of solid alkali perchlorates and sulfates, as well as of solid arsenic, antimony, and tin compounds, into the respective halides.[130] Such fuming reactions, some of them well known previously,[131] were

[125] M. SHEPHERD, Anal. Chem. 19, 77 (1947).

[126] Compare F. CUCUEL, Mikrochemie 13, 323 (1933), regarding the "aluminum test."

[127] E. SCHMIDT and E. TORNOW, Chem. Ztg. 56, 187, 206 (1932).

[128] F. FEIGL and L. BADIAN, unpublished studies. Compare also F. FEIGL, Spot Tests, p. 54.

[129] Strictly speaking, the activation of aluminum by mercury does not involve an heterogeneous catalysis since the catalyzer (Hg) forms a common phase (amalgam) with one of the reaction components.

[130] Considerable practical importance attaches to the possibility of converting SnO_2 into volatile SnI_4 by heating with NH_4I. E. R. CALEY and M. G. BURFORD, Ind. Eng. Chem., Anal. Ed. 8, 114 (1938), have shown that this conversion proceeds quantitatively and provides a convenient possibility of isolating contaminants and admixed materials from SnO_2. See also p. 649.

[131] The volatilization of arsenic from alkaline earth arsenates by fuming with ammonium chloride was described long ago by H. ROSE, Z. anal. Chem. 1, 417 (1862).

studied experimentally by Moser[132] and their theoretical bases elucidated by him. These changes involve the reaction possibilities of the dissociation products of the thermal decomposition of ammonium halides. The first point to be considered is the thermal dissociation

$$NH_4X \rightleftharpoons NH_3 + HX \qquad (X = Cl, Br, I) \qquad (1)$$
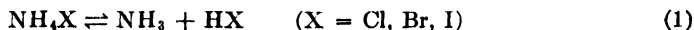
which leads to anhydrous, very reactive halogen hydracids. At the working temperature, a second point must be taken into account, namely the decomposition of the ammonia, produced in (1), which leads to the equilibrium

$$2NH_3 \rightleftharpoons N_2 + 3H_2 \qquad \qquad (2)$$

Finally, the thermal dissociation of HX

$$2HX \rightleftharpoons H_2 + X_2 \qquad (3)$$

must also be considered. This can be disregarded in the case of HCl; it is slight with HBr, but considerable with HI (approx. 18% at 450°C.).

Accordingly, when ammonium halides are used in fuming-off procedures, a continuing source of halogen hydracid and hydrogen is provided. The dissociation products of ammonia clear up the catalytic effect observed by Blangey.[133] He found that if potassium chlorate is mixed with about four times as much ammonium chloride and then heated in a porcelain crucible, the conversion into potassium chloride is still incomplete after the process has been repeated ten times. In contrast, the conversion is quantitative after the second fuming if the reaction is conducted either in a platinum crucible, or in a porcelain crucible in the presence of platinum chloride (approx. 0.05 mg. for 0.5 g. KClO$_3$). The platinum catalyzes this reaction because it brings about rapid establishment not only of the ammonia equilibrium but also of that between molecular and atomic hydrogen. The potassium chlorate is quickly reduced to chloride by the active atomic hydrogen, which is rapidly replenished through the agency of the metallic platinum. Consequently, in the presence of platinum, the thermal dissociation of ammonium chloride provides a strong, i.e., a quick acting reducing agent.[134] The same is true of ammonium bromide and iodide. Dissociating ammonium iodide is inherently a stronger reducing agent than

[132] L. MOSER, Monatsh. 53, 39 (1929); L. MOSER and S. MARIAN, Ber. 59. 1335 (1926).

[133] L. BLANGEY, Chem. Ztg. 43, 691 (1919).

[134] The acceleration of reducing reactions with ammonium halides requires relatively large amounts of platinum in contrast to other catalyzed reactions in which even traces of a catalyst often suffice. This contrast is understandable if it be kept in mind that in fuming reactions with ammonium halides the site of the catalysis is the solid/solid contact surface.

the chloride or bromide, because the relatively extensive dissociation of hydrogen iodide provides an additional source of hydrogen. Accordingly, it was not surprising when it was found that barium sulfate is readily converted into barium iodide by heating ·with ammonium iodide.[135]

In the foregoing examples of heterogeneous catalysis, one of the participants invariably was a gas while the other was in either the solid or the dissolved state. An excellent instance in which a solid catalyzes a change in a dissolved material is the decomposition of hydrogen peroxide solutions when they are placed in contact with higher metal oxides (MnO_2, PbO_2, etc.), or the corresponding oxyhydrates. The activity of higher oxides is explained by assuming that they are reduced to lower oxides by the hydrogen peroxide, and subsequently reoxidized to the original oxide. For instance, the following scheme can be given in the case of MnO_2:

$$MnO_2 + H_2O_2 \rightarrow MnO + H_2O + O_2. \ldots \qquad \text{(1) rapid)}$$
$$MnO + H_2O_2 \rightarrow MnO_2 + H_2O \qquad \ldots \qquad \text{(2) (rapid)}$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad \text{(1) + (2) rapid}$$
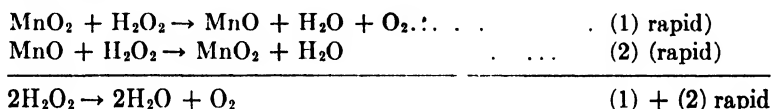
Summation of (1) and (2) gives the equation for the decomposition of hydrogen peroxide, which of itself is slow, but which proceeds at a high rate if the two rapid reactions are combined.

The behavior of $Ni(OH)_2$ and $Ni(OH)_4$ toward ‚hydrogen peroxide deserves special attention. The former is not noticeably oxidized to $Ni(OH)_4$ by hydrogen peroxide; instead, rapid and complete decomposition of the hydrogen peroxide occurs on warming. In contrast, black $Ni(OH)_4$, that has been prepared by treating $Ni(OH)_2$ with alkali persulfate or bromine water, is not stable toward hydrogen peroxide, but is reduced almost immediately to green $Ni(OH)_2$. Accordingly, the catalytic decomposition of hydrogen peroxide on contact with $Ni(OH)_2$ must obviously be ascribed to the intermediate production of a small amount of $Ni(OH)_4$, which is again reduced to $Ni(OH)_2$ by more peroxide. Consequently, the latter functions as catalyst. Feigl and his associates[136] have employed this heterogeneous catalysis to destroy any unused hydrogen peroxide that remains after oxidations carried out by means of alkaline peroxide. It is sufficient to add a little nickel salt solution and to bring to a boil.[137]

[135] F. FEIGL, D. GOLDSTEIN and N. CASTIELL, unpublished studies.

[136] F. FEIGL, K. KLANFER and L. WEIDENFELD, Z. anal. Chem. **80**, 5 (1925).

[137] This procedure is of practical value in the analysis of chrome tanning liquors. The Cr^{III} salts are oxidized by alkaline hydrogen peroxide to chromate and the latter then measured iodometrically. In the presence of gelatine and colloidally dispersed hide substance, the decomposition of alkaline peroxide is incomplete even after prolonged boiling or concentration (compare V. KUBELKA and J. WAGNER, *Collegium*

Paal and Friederici[138] made some interesting discoveries that involve heterogeneous catalysis. They found that, in the presence of a palladium or platinum salt, metallic nickel is precipitated on warming a nickel salt solution with sodium hypophosphite or hydrazine (the latter in ammoniacal or tartrated alkaline solution). Normally, the reaction:

$$2Ni^{++} + H_2PO_2^- + 2H_2O \rightarrow 2Ni° + PO_4^{---} + 6H^+$$
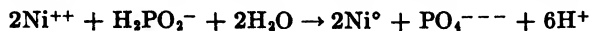
occurs only slowly and incompletely, with incidental production of varying amounts of nickel phosphide. Hydrazine does not react at all with nickel salts in ammoniacal or tartrated alkaline solution if platinum or palladium salts are absent. Consequently, the precipitation of metallic platinum or palladium by sodium hypophosphite or hydrazine induces the precipitation of nickel. Tanatar[139] proved that contact with spongy platinum causes alkaline hydrazine solutions to break down: $3N_2H_4 \rightarrow 2NH_3 + 2N_2 + 3H_2$. Paal and Friederici believe that this decomposition provides the hydrogen necessary for the reduction of nickel salts by hydrazine in the presence of platinum on palladium. Actually, sodium hypophosphite also decomposes in contact with finely divided platinum or palladium: $NaH_2PO_2 + 2H_2O \rightarrow NaH_2PO_4 + 2H_2$. Hence, it appears plausible to assume that it is this reaction which furnishes the hydrogen which, after activation on the platinum, reduces the nickel ion to the metal. According to this postulate, the catalyzed reduction of the nickel salts is due to free platinum produced by the action of sodium hypophosphite or hydrazine. The finely divided platinum then adsorbs these reducing agents and causes them to decompose with production of hydrogen.[140] Feigl and Fränkel[141] proved that the catalytically accelerated reduction of nickel salts by sodium hypophosphite can be used for the detection of traces of platinum and palladium. This precipitation of metallic nickel will reveal 0.0025γ Pd in 1 ml.; if 10 ml. of solution is taken, as little as 0.0015γ Pd can be detected. These figures correspond

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1926, 257). Consequently, the iodometric determination of the chromate yields false values. The stable linkage of the hydrogen peroxide to colloidal albuminous compounds is broken down through the catalytic decomposition of the peroxide in contact with $Ni(OH)_2$, and correct values for chromate are obtained.

[138] C. PAAL and L. FRIEDERICI, Ber. **64**, 1766 (1931); **65**, 19 (1932).

[139] S. TANATAR, Z. physik. Chem. **40**, 475 (1902); **41**, 37 (1902); compare also A. GUTBIER, ibid. **84**, 203 (1913).

[140] The explanation offered by Paal and Friederici is not the only possible one. The activated NaH_2PO_2 or N_2H_4 might of themselves be capable of reducing the nickel, i.e., without preliminary decomposition to yield hydrogen. An intermediate reaction catalysis in a homogeneous system is also possible. In this case, reduction of Pd^{++} ions would yield Pd^I, which as the reactive intermediate stage could reduce Ni^{++} ions with regeneration of Pd^{++} ions.

[141] F. FEIGL and E. FRÄNKEL, Ber. **65**, 540 (1932).

to the enormous dilutions 1:400,000,000 and 1:6,600,000,000, respectively. The catalytic effect of silver halides on redox reactions of hydrochloric acid (p. 123) and the decomposition of alkali hypobromite solutions by higher oxides of copper, cobalt, and nickel (p. 130) are likewise instances of heterogeneous catalysis. Special attention should be given here to the catalytic acceleration of the iodine-sodium azide reaction by soluble and insoluble metal sulfides (p. 126). The latter certainly present a case of heterogeneous catalysis.

A scrutiny of the foregoing examples of the analytical applications of heterogeneous catalysis shows that they have one characteristic in common, namely, that certain reactions take place on the boundary surface of the solid catalyst. Neither the interior of the catalyst nor the phase interior of the reactants (gas or liquid space) is directly involved in the reaction. The reactants are brought to the surface of the catalyst solely by diffusion, or the reaction products diffuse away from there. Hence, for this type of reaction, the term "contact catalysis" is more appropriate than "heterogeneous catalysis." Because of the localization of the seat of the reaction, contact catalysis is closely related to adsorption and to topochemical reactions. These topics are discussed in Chapters X and XI, respectively.

In contrast to the great number of catalyzed accelerations of reactions that can be used analytically, there are only two known cases in which a hindering of catalytic actions is applied for detection purposes. A typical masking is involved in the tests described by Feigl and Uzel[142] for telluric and periodic acids. The anions of these acids form complexes with copper[III] oxide and so inhibit its catalytic action in the conversion of manganese dioxide to permanganate. There is as yet no explanation of the interesting observation of Quartaroli[143] that the dehydration of blue $Cu(OH)_2$ to black CuO in alkaline suspension is accelerated by small quantities of hydrogen peroxide, and that this action can be prevented by even traces of magnesium salts. Both effects can be used to detect hydrogen peroxide or magnesium salts.

The great majority of catalyzed reactions that are of value to the analyst have, up to the present, been inorganic. Consequently inorganic materials particularly are detected by means of catalytic effects. There is no doubt, however, that catalyzed reactions may possess considerable importance in the qualitative analysis of organic compounds.

An excellent example is afforded by the catalytic acceleration of the iodine-sodium azide reaction (see p. 127) by organic compounds that contain the groups C=S or C—SH (thioketones and mercaptans).

[142] F. Feigl and R. Uzel, *Mikrochemie* **19**, 134 (1936).
[143] A. Quartaroli, *Chem. Abstracts* **30**, 4368 (1936).

This effect, discovered by Feigl,[144] provides a sure method of identifying these groups with a minimum quantity of test material, since free sulfur as well as other sulfur-containing compounds (thioethers, disulfides, sulfones, sulfonic acids) have no effect on the iodine-azide reaction. The mechanism of the action in the case of carbon disulfide has been proved to be an intermediate reaction catalysis.[145] As shown in (I), carbon disulfide and sodium azide form sodium azidodithiocarbonate,[146] which reacts with iodine to regenerate carbon disulfide (II). Summation of (I) and (II) gives the net equation (III) representing the catalyzed reaction, in which the catalyst CS_2 does not appear as a reactant:

$$CS_2 + NaN_3 \rightarrow SC\!\!\begin{array}{c} SNa \\ \diagdown \\ N_3 \end{array} \qquad \dots\dots\dots\dots\dots\dots\dots \text{(I)}$$

$$SC\!\!\begin{array}{c} SNa \\ \diagdown \\ N_3 \end{array} + I \rightarrow CS_2 + NaI + 3N \dots\dots\dots\dots\dots \text{(II)}$$

$$NaN_3 + I \rightarrow NaI + 3N \dots\dots\dots\dots\dots\dots\dots \text{(III)}$$
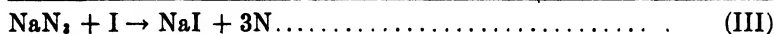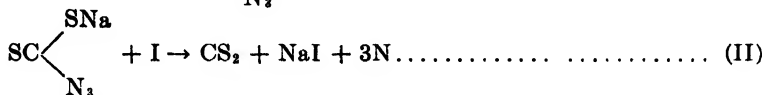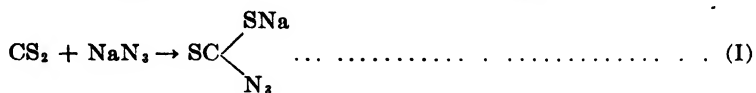
An analogous mechanism can be assumed for the catalytic action of thioketones. In contrast, the mechanism for mercaptans is more probably similar to that given in the discussion of the catalytic action of inorganic sulfides on this reaction (see p. 126).[147] G. Woker[148] made the interesting observation that the oxidation of p-phenylenediamine by hydrogen peroxide in neutral solution to a black quinoidal compound (Bandrowsky's base) is catalytically accelerated by aldehydes, which accordingly, here display the action of a peroxidase. Feigl and Frank[149] made this catalytic effect the basis of a sensitive test for aldehydes. It was found on carrying out the catalytic oxidation in neutral and acid solutions that aliphatic and aromatic aldehydes behave differently and can thus be distinguished. Frehden and Huang[150] showed that the decomposition of oxalic acid (at 100–110°C.) into formic acid and carbon dioxide can be used as a test for glycerol, which catalyzes this decomposition. Either the resulting CO_2 or the intermediate product, i.e.,

[144] F. FEIGL, *Mikrochemie* **15**, 1 (1934).

[145] F. FEIGL and E. CHARGAFF, *Z. anal. Chem.* **74**, 376 (1928).

[146] This compound is no hypothetical intermediate product. It has been isolated along with other heavy metal salts of azidodithiocarbonic acid. Compare F. SOMMER, *Ber.* **48**, 1833 (1915).

[147] Compare also E. FRIEDMANN, *J. prakt. Chem.* **146**, 179 (1936).

[148] G. WOKER, *Ber.* **47**, 1024 (1914); see also G. WOKER, Die Katalyse (Sammlung, Die Chemische Analyse, Vol. 27–28), p. 232. Berlin, 1931.

[149] F. FEIGL and G. FRANK, unpublished studies; compare F. FEIGL, Spot Tests, p. 345.

[150] O. FREHDEN and C. HUANG, *Mikrochim. Acta* **2**, 20 (1937).

monoform (monoformic ester of glycerol), can be tested for. The specific action of enzymes, which is revealed in characteristic decompositions or degradations of definite substrates, has been used by Sastri and Screenivasaja[151] for detecting enzymes. The tests are based on the detection of the alterations in the substrates, brought about by the enzymes. Urease, zymase, emulsin, lipase, proteases, catalases, and peroxidases, can be detected definitely by such spot reactions.

The few instances in which analytical use has been made of the catalytic acceleration due to the action of light (photocatalysis) are found in qualitative organic analysis. The tests for nitroso compounds and for certain alkaloids (see pp. 689, 691) belong in this category. The available examples indicate plainly that further study of the application of catalytic reactions will reveal much that will be valuable in the field of qualitative organic analysis.

The analytical importance of catalyzed and induced reactions rests on the fact that such effects can be brought about by very small quantities of material, and that the actions are confined to definite reaction systems. Consequently, their analytical employment is in line with the effort to attain the maximum certainty and sensitivity. However, the participation of catalysts in reactions always conforms to chemical principles, and consequently their catalytic effects are never unlimited. They cease at certain, usually very minute, quantities of the catalyst. It is often possible to prove that catalytic effects, within certain limits, are proportional to the concentration of the catalyst.

INDUCED PRECIPITATION AND INDUCED SOLUTION

In many precipitation reactions the precipitate contains attendant materials which, of themselves, either do not react with the precipitant at all or only react slowly. Such coprecipitated compounds frequently exhibit solubility anomalies. On the other hand, insoluble materials are sometimes simultaneously brought into solution when soluble substances are also present. These phenomena, known as *induced precipitation* and *induced solution*, respectively, have a certain formal similarity to the induced reactions discussed in the previous section. In induced precipitations, usually one ion (the actor) is common to the pure precipitate and the coprecipitated material. The opposite ion of the pure precipitate is the inductor, that of the coprecipitated material is the acceptor. The induction factor of induced precipitations, in contrast to that of true induced reactions (see p. 132), is usually small, frequently much less than 1. The terms "induced precipitation" and "induced solution"

[151] N. SASTRI and M. SCREENIVASAJA, *Mikrochemie* 14, 159 (1933-34). See also F. FEIGL, Spot Tests, p. 421.

at present are simply collective names for various processes, such as occlusion, adsorption, and the formation of chemical compounds, isomorphic mixtures, solid solutions, mixed crystals, colloidal solutions, *etc.* Frequently, it is impossible to separate such occurrences; often they proceed concurrently or in sequence. Since they usually depend greatly on numerous details of the conditions of the precipitation or solution, it is often difficult to reproduce them and, consequently, they do not readily lend themselves to intensive investigation. Valence forces, of the same kind that predominate in coordination compounds, probably play an essential role in many induced precipitation and solution reactions. A knowledge of the activity of such forces was, of course, derived from definite complex compounds, but to limit the acceptance of these forces to compounds that can be isolated would hardly be proper.

No matter what explanation is given for the partial processes of induced precipitation and solution reactions, the effects of these peculiar phenomena are of prime importance to analytical chemistry. They are responsible for the fact that the limits of the applicability of analytical methods must still, to a large extent, be determined empirically. Absolute certainty of analytical methods of detection and determination is practically never attained. More or less serious interferences are constantly encountered, and many of the various guises of induced precipitation and solution are in this class. Induced precipitations are the most frequent sources of error in analytical determinations. Predictions about their intervention or extent can hardly ever be made. Only their effects are registered and these can be recognized by the fact that the precipitates obtained usually are not identical with a mere mixture of their constituents. This difference is shown by their behavior in chemical reactions. Induced precipitation and solution reactions are, however, not always sources of error that must be avoided, if possible. Occasionally they can be used beneficially for purposes of qualitative and quantitative analysis. Pertinent examples will be given later.

A model example of the occurrence and the behavior of an induced precipitation if afforded by the pair $BaSO_4$-$CaSO_4$. Calcium is not precipitated from dilute solutions by sulfuric acid, and, when precipitated from concentrated solutions, the $CaSO_4$ is easily soluble in sodium thiosulfate. If, however, barium is precipitated with sulfuric acid in the presence of calcium, the $BaSO_4$ always contains calcium, even though no more than small quantities of the latter are present. Furthermore, the $CaSO_4$ cannot be removed from the precipitate either by persistent washing with water or sodium thiosulfate.[152] The tendency of barium sulfate to "carry down" numerous other materials present in the solu-

[152] R. FRESENIUS, *Z. anal. Chem.* **30**, 458 (1891).

tions from which it is precipitated is well-known and must always be kept in mind when determining barium or sulfate. For instance, if $BaCl_2$ is added to an acidified solution that contains phosphate along with sulfate, the $BaSO_4$ will contain $Ba_3(PO_4)_2$ or acid barium phosphates, despite the fact that PO_4^{---} is normally not precipitable by Ba^{++} in acid solution. The extent of the coprecipitation of the barium phosphate depends on the precipitation conditions. It is least when the barium chloride is added dropwise to the boiling solution.[153] There is an extensive literature on this phenomenon.[154] The selective character of the precipitation of $CaSO_4$ induced by $BaSO_4$ is noteworthy because it prevents the carrying down of other salts.[155] If sulfate is precipitated in the presence of ferric or cobalt salts, the barium sulfate contains much iron or cobalt[156] as revealed by the bright yellow or bluish violet color of the precipitate. The iron is so firmly bound that it is not removed, even by boiling for hours with concentrated hydrochloric acid. However, barium sulfate absolutely free of iron and cobalt is obtained if calcium salts are also present. Consequently, the coprecipitation of iron and cobalt is prevented by the induced precipitation of $CaSO_4$.

Induced precipitations in the deposition of metal salts of organic acids are exemplified by the precipitation of iron by α-nitroso-β-naphthol. This operation must be carried out in the cold if chromic salts are present; otherwise, even in hydrochloric acid solution, the precipitate contains considerable chromium. The latter, when by itself, is not precipitated from hydrochloric acid solution by this reagent. Likewise, the determination of manganese by precipitation with alkali phosphate suffers from the fact that zinc, nickel, copper, and other metal salts enter the manganese precipitate even though they are not precipitated from an ammoniacal ammonium chloride solution by phosphate when unaccom-

[153] P. PIERRON, *Compt. rend.* **216**, 185 (1945).

[154] The ability of $BaSO_4$ to carry down all manner of substances from either true or colloidal solutions can in many cases be considered as adsorption. There is no doubt, however, that $BaSO_4$ is capable also of forming mixed crystals. See p. 162 and also H. B. WEISER's paper "Adsorption by Precipitates" in Colloid Chemistry (edited by J. Alexander), Vol. 1, p. 600, New York, 1926; also A. CLASSEN, Ausgewählte Methoden der analytischen Chemie, Vol. 2, p. 305, 1903, and I. M. KOLTHOFF and E. H. VOGEL-ENSANG, *Pharm. Weekblad.* **56**, 122 (1919).

[155] M. VAN'T KRUYS, *Z. anal. Chem.* **49**, 393 (1910).

[156] G. SMITH [*J. Am. Chem. Soc.* **39**, 1152 (1917)] assumes that such contamination of $BaSO_4$ is not due to a solid solution of basic ferric sulfate or another compound, nor to adsorption, but because a complex salt, $BaFe(SO_4)_2$ is present in an intimate mechanical mixture with the barium sulfate. If $FeCl_3$ is present, iron is adsorbed by the other alkali earth sulfates also, as well as by calcium oxalate and citrate. R. DAHR, K. SEN and N. CHATTERJI, *Kolloid-Z.* **33**, 29 (1923).

panied.[157] The behavior of copper salts in the precipitation of iridium or bismuth salts by a potassium bromate-bromide mixture (precipitation of $IrO_2 \cdot aq$ or basic bismuth salt) is very interesting. The IrO_2 can carry down almost all of the copper, whereas the precipitation of bismuth exerts no observable action.[158] Studies of the deposition of free tellurium from tellurites and tellurates by sulfur dioxide show that induction effects are not limited to the precipitation of metal salts. If heavy metals are present they are partially carried down with the tellurium (obviously because of adsorption). This is particularly true of copper,[159] where the quantity coprecipitated depends on the length of time the sulfur dioxide acts. Copper is also carried down, even though present in only small quantities, when selenium is liberated from selenite solutions by sulfur dioxide.[160]

Many instances of induced precipitation that may be regarded as reaction abnormalities occur with sulfides. Since sulfide precipitations are so often employed in analytical separations, a knowledge of the sources of errors that may arise from induced precipitations is of special practical importance here. Consequently, several reaction anomalies of this type will be discussed.

If CuS is precipitated from strong acid solutions in the presence of cadmium the latter is coprecipitated.[161] The same is true of zinc.[162] Despite the presence of much acid, HgS can carry down CuS and CdS; likewise FeS coprecipitates with CuS, even in 3 normal hydrochloric acid solution.[163] When ZnS is precipitated from acetic acid solution it causes partial coprecipitation of MnS, CoS, NiS, and FeS, even though these sulfides normally cannot be precipitated from acetic acid solution.[164] ZnS is coprecipitated in acid solution with As_2S_5,[165] and with CdS.[166] Although Tl_2S cannot be produced in mineral acid solution, it is partially coprecipitated at the formation of the sulfides of As, Sb, Sn, Hg, Cu, and

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[157] L. L DE KONINCK, Lehrbuch der qualitativen und quantitativen Analyse, (revised by C. Meinecke and A. Westphal) 1, p. 491. Berlin, 1904.

[158] L. MOSER and H. HACKHOFER, *Monatsh.* 59, 57 (1932).

[159] B. BRAUNER and B. KUZMA, *Ber.* 40, 3362 (1907).

[160] Private communication from L. MELNIK, Ghent.

[161] E. BERGLUND, *Z. anal. Chem.* 23, 184 (1883).

[162] K. SCHERINGA, *Pharm. Weekblad* 57, 1289 (1918); I. KOLTHOFF and J. VAN DIJK, *Chem. Weekblad* 59, 1351 (1922).

[163] W. BÖTTGER, *Z. angew. Chem.* 38, 802 (1925).

[164] W. FUNK, *Z. anal. Chem.* 46, 93 (1907). Concerning the coprecipitation of CoS and of FeS from formic acid solution see P. v. BERG, *ibid.* 25, 512 (1896).

[165] DE KONINCK-MEINECKE, *op. cit.*, vol. 2, p. 178. Berlin, 1904.

[166] W. TREADWELL and H. GUITERMANN, *Z. anal. Chem.* 52, 459 (1913); see also O. FOLLENIUS, *ibid.* 13, 428 (1874).

Pb.[167] SnS_2 carries down, in acid solution, FeS and CoS; and SnS coprecipitates considerable quantities of NiS.[168] Tungsten sulfide is partially coprecipitated in the presence of cations, such as Mn^{++}, that can be precipitated by $(NH_4)_2S$, even though WS_3 is easily soluble in alkali sulfides with formation of sulfotungstate. Platinum sulfide is incompletely precipitated from acid solution by H_2S; nevertheless, PtS_2 induces the sulfide precipitation of metals that otherwise are not precipitated at all from acid solution. Iron is particularly coprecipitated in this way. Uslar[169] made the interesting observations that the addition of solid ammonium chloride to a sulfo-alkaline solution of Na_2HgS_2 and Na_2SnS_3 causes precipitation of HgS containing SnS_2, and that a part of the mercury, which when alone is precipitated quantitatively, remains in the solution of the thiostannate.[170]

Induced precipitation can thus produce, through coprecipitation, sulfides that normally are not formed·under the particular conditions. On the other hand, concurrently precipitated sulfides often have characteristics which indicate that they are not merely intermixed. Frequently, they exhibit reaction anomalies of the same type as these shown by the other precipitates produced by induced precipitation. Several examples[171] selected from the author's own studies, will illustrate this behavior.

It is well known that NiS cannot be precipitated from acid solutions by hydrogen sulfide. Nevertheless, the precipitate that has been produced in an alkaline medium is not soluble in dilute mineral acids. However, if nickel sulfide is coprecipitated with lead sulfide by means of ammonium sulfide, considerable quantities of NiS can be dissolved by dilute acid from the mixed precipitate, and when precipitated with a large excess of lead sulfide, the NiS is almost quantitatively soluble in dilute mineral acids. Consequently, coprecipitation of NiS with excess PbS does not produce a mere physical mixture of the two sulfides.

MnS dissolves easily in dilute acetic acid, but when it is coprecipitated with the sulfides of zinc, mercury, or cadmium,[172] much of it remains with the undissolved sulfide after the precipitate is digested with acetic

[167] J. LOCZKA, *J. Chem. Soc.* **76**, II, 100 (1899); L. HAWLEY, *J. Am. Chem. Soc.* **29**, 1011 (1907); L. BRUNER and J. ZAWADSKI, *Z. anorg. allgem. Chem.* **65**, 136 (1909).

[168] L. STORCH, *Ber.* **16**, 2014 (1883); compare V. ANGER and L. ODINOT, *Compt. rend.* **178**, 710 (1923).

[169] C. USLAR, *Z. anal. Chem.* **34**, 391 (1895).

[170] Compare T. WILM, *Z. anal. Chem.* **28**, 99 (1889).

[171] F. FEIGL, *Z. anal. Chem.* **65**, 25 (1924); *Z. anorg. allgem. Chem.* **157**, 251, 257 (1926).

[172] H. SCHNAASE [*Z. physik. Chem.* **20**, B, 89 (1933)] has established, by means of X-rays, the formation of the mixed crystals MnS-CdS and MnS-ZnS.

acid and then washed with water. A similar result is obtained if particles of HgS are coated with MnS, thus excluding the possibility that MnS is shielded from the dissolving acid by the formation of a protective film of HgS. If the manganous solution is added to HgS suspended in $(NH_4)_2S$, it is not possible subsequently to extract the MnS from the precipitate by digestion with 20% acetic acid, although, when alone, MnS is easily soluble in acid that is much more dilute. MnS precipitated on freshly precipitated HgS, or on HgS aged in suspension, shows a remarkable stability toward even mineral acids. The abnormal stability toward acids of MnS precipitated along with ZnS, CdS, or HgS has a counterpart, to a certain extent, in the anomalous behavior of other pairs of sulfides. This has been shown with HgS, but not with ZnS and CdS, probably because no suitable reaction has been found. HgS dissolves easily in Na_2S to form Na_2HgS_2, whereas when coprecipitated with MnS, ZnS, or CdS, it loses this solubility to a considerable degree. About 50% of the mercury sulfide is retained if the surface of 26 mg. of freshly precipitated, flesh colored MnS is covered with a film of HgS by digesting it with 20 ml. of $M/25$ $HgCl_2$, and then treating the suspension with strong warm Na_2S solution until the filtrate no longer gives a precipitate of HgS when acidulated. If the experiment is duplicated with the green modification of MnS, only about 10% of the mercury is retained. Even greater quantites (up to 70%) of HgS are prevented from dissolving in Na_2S, if equimolar quantities of CdS are used in place of MnS; ZnS also can retain considerable quantities of HgS. The incomplete solubility of HgS in Na_2S in the presence of MnS, CdS, or ZnS, can be easily recognized, even without analysis, by the abnormal colors of the residual sulfides. This phenomenon is observed also if a solution of $HgCl_2$ is run, with warming, into a solution of Na_2S carrying suspended MnS, CdS, or ZnS. Not only is Na_2HgS_2 formed, but orange-red, lemon-yellow, or brown precipitates, containing considerable quantities of HgS, result. If the amounts of metal sulfide suspended in the concentrated Na_2S solution are raised, increasing proportions of HgS are retained. At a ratio HgS:CdS = 1:8, about 90% of the mercury of 20 ml. $N/2$ $HgCl_2$ is prevented from dissolving in Na_2S, an amount far above the order of the quantity of material that can be taken up by adsorption. It is probable that mixed sulfides of the type $Me[HgS_2]$ are formed. They (Me = Cd, Mn, Zn) can be regarded as derivatives of the soluble $Na_2[HgS_2]$. Finally, it should be mentioned that Röll[173] found that vanadium sulfide coprecipitated with FeS or MnS, in contrast to pure V_2S_5, is difficultly soluble in ammonium sulfide.

Although the phenomena have long been known through isolated

[173] F. Röll, *Z. anal. Chem.* **74**, 342 (1928).

observations, the induced precipitation of sulfides and the abnormal behavior of coprecipitated sulfides have only recently been given special attention. New experimental material has been found and illustrative experiments have been made,[174] though it must be admitted that the findings have not sufficed to explain satisfactorily the selective character and the quite varying extent of these reaction anomalies. It seems necessary to take account of different partial processes that proceed concurrently and to varying degrees. Kolthoff and his collaborators[175] have made an important contribution by proving that the precipitation of ZnS, induced by CuS and HgS, and the precipitation of FeS, induced by CuS, are to be ascribed not to a simultaneous coprecipitation, as was formerly believed, but to a post-precipitation by H_2S condensed on the primary precipitate. Possibly this is the most important fundamental process in the induced precipitation of sulfides from acid solutions (see p. 634). The ability of certain metal sulfides to induce the coprecipitation of their cosolutes and the abnormal analytical behavior of certain mixtures of sulfides that have been precipitated together, are very probably related to the gel-like structure of sulfides produced by the wet method. This structure permits the binding powers that reside in the extensive free surface to come into action. A likely consequence is adsorption and, therefore, concentration or condensation of metal and sulfide ions (or H_2S), which normally do not combine at the prevailing pH. However, when adsorbed, they unite to form a sulfide which, in the nascent state, can combine with the primary precipitated sulfide to form mixed crystals, adsorption compounds, or true complex compounds with fixed stoichiometric formulas. The most important causes of the reaction anomalies exhibited by sulfides precipitated together will probably be found in the union of sulfides through the action of intermolecular linkages.

The assumption that the gelatinous nature of sulfides plays an important part in induced precipitations is supported by examples of such precipitations among the amorphous gel-like metal hydroxides or hydrated oxides. Typical instances are provided by studies of the separation of ferric iron from aluminum and zinc by means of excess sodium hydroxide, and the separation of ferric iron by means of ammonium hydroxide (in the presence of ammonium salts) from manganese, zinc, nickel, or cobalt. The hydrated ferric oxide always retains considerable amounts of the

[174] Compare F. FEIGL, *Z. anal. Chem.* **65**, 25 (1925); *Z. anorg. allgem. Chem.* **157**, 251, 269 (1926); O. RUFF and B. HIRSCH, *ibid.* **151**, 81 (1926); O. RUFF, *ibid.* **185**, 387 (1930); W. BÖTTGER and K. DRUSCHKE, *Ann.* **453**, 315 (1927).

[175] I. M. KOLTHOFF and E. PEARSON, *J. Phys. Chem.* **36**, 549 (1932); I. M. KOLTHOFF and F. S. GRIFFITH, *J. Am. Chem. Soc.* **60**, 2036 (1938).

cosolute, even though the latter, when alone, cannot be precipitated by excess alkali or ammonia.   Likewise, the separation of copper and zinc by means of an excess of sodium hydroxide is never quantitative, because the hydrous copper oxide always contains zinc.   Scheringa[176] made the interesting observation that, when hydrous ferric oxide is precipitated with strong caustic, the suspension in this liquid always takes up zinc from the alkali zincate, even if the zinc salt is added after the iron has been thrown down.   The amounts of contaminating oxide (or hydroxide), which are carried down by the hydroxide precipitate, depend, as might be expected, on the relative proportions in which the two metals were originally present in the solution.[177]   This was shown plainly by Yasni[178] who found that a solution containing chromium and zinc (in the ratio 1:11) produces, with ammonia, a precipitate whose zinc content is 1.5 times as great as that of the Cr_2O_3.   Toporescu[179] found that the amount of CaO or MgO precipitated along with $Cr_2O_3 \cdot aq$ increases as the relative quantity of calcium or magnesium in the solution rises.   It approaches a limit corresponding to the chromites $Cr_2O_3 \cdot 3CaO$ and $Cr_2O_3 \cdot 3MgO$, respectively.   The tendency to form a compound during an induced precipitation is shown distinctly in these cases.

Induced precipitations also include the following phenomenon.   A masking agent normally prevents the precipitation of an ionic or molecular species.   However, the masking agent may be ineffective in the presence of cosolutes that are indifferent to it.   Examples of this are given in Chapter IV.

Induced solution is not as common as induced precipitation.   Among the sulfides, coprecipitated mercuric and tin sulfides, on digestion with ammonium sulfide, not only form a solution of $(NH_4)_2SnS_3$, but considerable quantities of mercuric sulfide also dissolve.   This occurs despite the fact that HgS when alone, and also in mixtures with other sulfides, is completely insoluble in ammonium sulfide.[180]   A more instructive example is $Co(OH)_3$.   In contrast to $Ni(OH)_2$, it is insoluble in potassium cyanide, but a mixture of the two dissolves easily in this

[176] K. Scheringa, *Pharm. Weekblad* **60**, 39 (1923).

[177] In qualitative analysis, these separations by precipitation of hydroxides are quite satisfactory, provided large quantities of materials, present in approximately equal proportions, are involved.   If the relative proportions are quite unequal, considerable losses may occur as a result of induced precipitations.   In quantitative analysis, hydroxide separations should be avoided whenever possible, or the error should be reduced to a minimum by repeated solution and reprecipitation.

[178] T. Yasni, *Mem. Coll. Sci. Kyoto Imp. Univ.* **4**, 65 (1920); *Chem. Abstracts* **15**, 997 (1921).

[179] E. Toporescu, *Compt. rend.* **172**, 600 (1921).

[180] A. Classen, Ausgewählte Methoden **1**, p. 116.   Brunswick, 1901.

reagent.[181] Beryllium can be precipitated by phosphate as $BeNH_4PO_4$, even in the presence of citric acid. However, its precipitation is prevented if considerable quantities of aluminum salts are present. Conversely, when beryllium hydroxide dissolves.in ammonium carbonate, a small part of any aluminum hydroxide is also carried into solution. An induced solubility likewise appears in the behavior of iron and chromium hydroxides toward caustic alkalies. Dilute alkali readily dissolves freshly precipitated $Cr(OH)_3$, but practically no $Fe(OH)_3$. However, a solution that contains considerable chromic salt along with ferric salt remains perfectly clear after the introduction of a liberal amount of caustic alkali. Knoche[182] showed that the solutions thus obtained have the characteristics of colloidal solutions (mixed sols). There is no doubt that $Fe(OH)_3$ is peptized by the alkali chromite. It is interesting that the peptizing effect of the chromite can be overcome, since flocculation of the $Fe(OH)_3$ occurs if the iron content is more than 40%. In this event there is coprecipitation of both hydroxides, induced by $Fe(OH)_3$. Knoche demonstrated that $Cr(OH)_3$ can likewise induce the solution of the other hydroxides (Co, Ni, Mg, Mn, Tl, Cu, Cd) in caustic solution. Those hydroxides that are less soluble than $Cr(OH)_3$ are dissolved the more easily, while the induced solubility of the more soluble ones is, without exception, small. It is particularly remarkable that other amphoteric hydroxides, such as $Al(OH)_3$ or $Zn(OH)_2$, are not capable of acting as $Cr(OH)_3$ does. Consequently, the exceptionally great ability of the chromium atom to form complex compounds is probably connected with its inducing action or with the peptizing effect.

Induced solution, like induced precipitation, usually involves a specific action of certain materials. This is seen in the anomalous solubility of noble metals in acids. For instance, compact rhodium is insoluble in acids. If alloyed with copper or platinum, it dissolves completely in aqua regia or, when alloyed with bismuth in the ratio 1:20, even in 50% nitric acid.[183] Alloying with silver or gold has no effect on the solubility of rhodium. Platinum and palladium do not dissolve in nitric acid, but when alloyed with other metals, silver particularly, they become markedly soluble in nitric acid. In fact, platinum dissolves quantitatively when alloyed with more than four times its weight of silver. Alloys display solubility abnormalities of another kind, namely resistance of one of the constituents of the alloy to solvents by which it

[181] Th. W. FRESENIUS, Qualitative Chemical Analysis (translated by C. Mitchell) New York, 1921, p. 239.

[182] H. KNOCHE, *Kolloid Z.* **67**, 195, 307 (1934); **68**, 37 (1934).

[183] H. RÖSSLER, *Chem. Ztg.* **24**, 734 (1901); compare L. WÖHLER and L. METZ, *Z. anorg. allgem. Chem.* **149**, 310 (1925).

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[183] H. Rössler, *Chem. Ztg.* **24**, 734 (1901); compare L. Wöhler and L. Metz, *Z. anorg. allgem. Chem.* **149**, 310 (1925).

is usually attacked.   For instance, chromium and iron, singly, are easily soluble in dilute HCl, but ferrochrome is exceedingly hard to bring into solution.   Still more resistant are the "stellites," which are alloys containing Co, Cr, Fe, Mo, and W.   Certain alloys, particularly some special steels, no longer dissolve in acids if they contain considerable quantities of Cr, V, Si, Ti, and other metalloids.   The observations of Tammann[184] are of great importance to metallurgy.   He found that many alloys have sharply defined limits beyond which an agent that can attack only one of the two components cannot act.   These "Tammann resistance limits" lie at simple atomic ratios.   For instance, if Au-Ag alloys are exposed to HNO_3, which ordinarily dissolves silver but not gold, the former is completely removed from all alloys whose composition ranges from pure silver down to 37.5 atom-% gold.   The quantity of silver dissolved decreases rapidly from 37.5 to 50 atom-% Au, and no silver at all is dissolved out of alloys still richer in gold (e.g., 1 part Au to 0.5 part Ag).   Accordingly, nitric acid dissolves silver from the Au-Ag mixed crystals only when the gold content is below a certain limit (in this case exactly at $\frac{3}{8}$ atom-% Au).   Up to that point the unattacked gold protects the baser silver from chemical attack.   Gold-copper alloys behave analogously toward nitric acid.

The instances of induced solution include also the rather remarkable phenomenon, discovered by Czerwek,[185] that tin, which is converted into insoluble stannic acid by a mixture of tartaric and nitric acid, forms a clear solution if antimony is also present (see p. 77).   Long ago, Rose observed that the presence of iron interferes with the conversion of tin into metastannic acid.   Lepez and Storch[186] found that tin dissolves in nitric acid, even at the ratio Fe:Sn = 1:1.   This effect is all the more remarkable because small quantities of iron do not impede the conversion of tin into metastannic acid, and are retained by this compound through adsorption (see p. 472).   Another instance that can be viewed as an induced solution is the fact that anhydrous chromic chloride, which is completely insoluble in water and acids, dissolves readily in dilute acid if zinc, magnesium, and other metals are taken into solution along with it.   Probably chromous chloride is formed by the nascent hydrogen produced when the metal dissolves.   Partial reactions (I) and (II) occur, and their summation shows the hydration and solution of $CrCl_3$:

$$CrCl_3 + H° \rightarrow CrCl_2 + H^+ + Cl^- \dots\dots\dots\dots\dots\dots (I)$$
$$CrCl_2 + 4H_2O + H^+ \rightarrow [Cr(OH_2)_4Cl_2]^+ + H° \dots \dots\dots\dots (II)$$

$$CrCl_3 + 4H_2O \rightarrow [Cr(OH_2)_4Cl_2]^+ + Cl^- \dots\dots\dots\dots\dots (III)$$
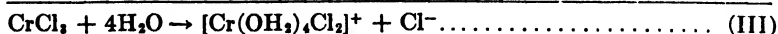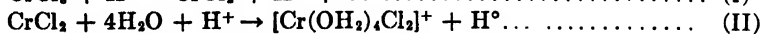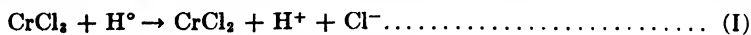
[184] G. Tammann, Z. anorg. allgem. Chem. 107, 1 (1919).
[185] A. Czerwek, Z. anal. Chem. 45, 505 (1906).
[186] C. Lepez and L. Storch, Monatsh. 10, 283 (1910).

Accordingly, the induced solution of chromic chloride can be considered really as a catalyzed reaction in an heterogeneous system (with $CrCl_2$ as catalyst). In fact, the addition of small quantities of $CrCl_2$ actually does bring about the solution of $CrCl_3$, with evolution of heat and formation of green $[Cr(OH_2)_4Cl_2]Cl$.[187] Lang[188] described a peculiar phenomenon that can be regarded as induced solution with simultaneous anomalous oxidation. He found that MnO_2 and excess NiO_2, if coprecipitated by alkaline persulfate, form permanganate and Ni^{II} salts on digestion with dilute nitric or sulfuric acid. This is noteworthy because MnO_2 normally is resistant to these acids, and MnO_2 and NiO_2 precipitated separately and then mixed show no irregular behavior toward them. The unexpected formation of MnO_4 probably is due to the fact that the atomic oxygen formed by the solution of higher nickel oxides has MnO_2 presented to it at the site of its production, and so it can bring about the conversion into MnO_4^- ion. This assumption is supported by the fact that other higher metal oxides (Co_2O_3, CeO_2, Tl_2O_3, and PbO_2) precipitated along with MnO_2 exhibit this same behavior.[189]

The anomalies that have been cited may give the impression that induced solubility reactions are limited to metals or their compounds. This is not the case. Several instances can be cited which plainly show that nonmetals and compounds of nonmetals can undergo induced solution. Free tellurium is not soluble in alkali sulfide solution, in contrast to sulfur and selenium, which dissolve to form alkali polysulfide and selenosulfide, respectively. Feigl and West[190] showed that tellurium is carried along into solution when its mixtures with sulfur or selenium are warmed with alkali sulfide solutions. The solution of the sulfur or selenium in alkali sulfide can thus be said to induce the solution of the tellurium. Correspondingly, tellurium is soluble in solutions of alkali polysulfide or selenosulfide. A solution containing both sulfur and tellurium has the characteristic yellow color of polysulfide solutions; the selenium-tellurium solutions, like selenosulfide solutions, are red-brown. The presence of tellurium in these solutions is readily revealed by gently warming a test portion that has been treated with alkali sulfite. Free tellurium precipitates quantitatively. This behavior sheds some light on the chemistry of the induced solution. Alkali sulfite is a known reagent for loosely bound sulfur or selenium; thiosulfate or selenosulfate results. Accordingly, it may be safely assumed that the inductively

[187] For the literature on this see R. Abegg, Handbuch der anorganischen Chemie., Vol. 4, p. 76. Leipsic, 1921.

[188] R. Lang, *Z. anorg. allgem. Chem.* **158**, 370 (1926).

[189] F. Feigl, unpublished studies.

[190] F. Feigl and P. W. West, unpublished studies.

dissolved tellurium is in loose combination with the sulfur or selenium. The following explanation of the solution of tellurium through the agency of sulfur seems quite plausible. The first stage is the formation of unstable tellurium disulfide:[191] $Te° + 2S° \rightarrow TeS_2$. This product dissolves in sodium sulfide: $TeS_2 + Na_2S + S° \rightarrow Na_2TeS_4$. Accordingly, the induced solution leads to the formation of sodium thiotellurite,[192] which is decomposed by sodium sulfite with precipitation of tellurium: $Na_2TeS_4 + 3Na_2SO_3 \rightarrow 3Na_2S_2O_3 + Na_2S + Te°$.

The induced solution of tellurium and the foregoing explanation are of significance with regard to systematic qualitative analysis. When hydrogen sulfide is passed into an acidified solution of metal salts in the presence of TeO_3^{--} ions, the precipitate of metal sulfide is accompanied by a mixture of tellurium and sulfur (compare[191]). On subsequent digestion with yellow ammonium sulfide to separate the "acid" sulfides, the tellurium will be inductively dissolved and thus carried into the arsenic group. The addition of acid to the resulting solution will precipitate free tellurium along with any arsenic, antimony, or tin sulfide, and thus make it necessary to use special methods to identify these metals. The foregoing precipitation of tellurium from alkali polysulfide solutions offers the possibility for separating tellurium from sulfides that form stable sulfo salts.[193]

An example of the induced solution of a non-metallic compound is due to Fischer and Stachel.[194] They found that phosphoric acid, which cannot be extracted by ether from aqueous solutions containing no ferric salts, is taken up from ferric chloride solutions, to varying degrees, if hydrochloric acid is also present. Likewise, Grahame and Seaborg[195]

[191] Several texts on analytical chemistry give the equation: $H_2TeO_3 + 2H_2S \rightarrow 3H_2O + TeS_2$ for the formation of tellurium disulfide. However, A. M. HAGEMAN [J. Am. Chem. Soc. 41, 329 (1919)] found that this demands qualification. The compound TeS_2 is stable only below $-20°C$.; at higher temperatures it decomposes into a mixture of its elements from which sulfur can be extracted with carbon disulfide. The present postulation of an immediate further reaction of the initially formed TeS_2 is not in conflict with its instability as a solid phase.

[192] A number of sulfotellurites have been prepared by other methods. See particularly, J. W. MELLOR, Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XI, p. 113 ff. New York, 1931.

[193] Free tellurium is precipitated quantitatively when a solution of an alkali tellurite is warmed with Na_2S and Na_2SO_3. The reactions are: $Na_2TeO_3 + 2Na_2S + 3H_2O \rightarrow 6NaOH + 2S° + Te°$ and $S° + Na_2SO_3 \rightarrow Na_2S_2O_3$. Selenites react with alkali sulfide analogously, but the resulting selenium is dissolved by Na_2SO_3 to produce stable Na_2SeSO_3. This differential behavior is the basis of a convenient procedure for separating selenium and tellurium in alkaline solution. Compare A. BRUKL and W. MAXYMOWICZ, Z. anal. Chem. 68, 16 (1928).

[194] W. FISCHER and F. STACHEL, Z. angew. Chem. 52, 368 (1939).

[195] D. C. GRAHAME and G. T. SEABORG, J. Am. Chem. Soc. 60, 2527 (1938).

found that isopropyl ether will extract more than half the phosphoric acid from solutions containing hydrochloric acid when ferric salts are present. It is possible that this induced solubility of phosphoric acid is connected with the formation of the complex ether-soluble $H[FeCl_4]$. It is likely that chlorine atoms of this compound can be replaced by their equivalent of phosphate radicals (compare footnote, p. 81).

Both induced precipitation and induced solution of compounds and elements are divergences from and anomalies of the normal course of chemical reactions. Consequently, they may bring about considerable errors in the conduct of qualitative and quantitative analyses and hence, for a long time, were invariably regarded as deleterious. Not until recently have a rather large number of instances shown that induced precipitation, at least, can be turned to advantage. In qualitative inorganic analysis this useful application may proceed along two lines. The first is direct in so far as the occurrence of an induced precipitation can be revealed through the production of an abnormal color or an abnormal precipitate. The second employment is indirect, in that a precipitation, which of itself is incomplete if it occurs at all, can be made quantitative by a simultaneous precipitation involving a cosolute. The second procedure is of special importance when traces of another dissolved material enter the precipitate. The reaction product of the inducing precipitation then serves as a trace catcher or collector for the product of the induced precipitation. The great importance of such collector action in the solution of microchemical problems or trace analysis need hardly be emphasized.[196] The following examples illustrate the analytical employment of induced precipitation in its various forms.

Zirconium salts react in acid solution with arsenic acid to form colorless neutral or acid zirconium arsenates. Under these conditions, titanium salts precipitate only slowly, and the precipitation becomes less complete as the acidity and dilution of the solution rise. Feigl and

[196] The application of collector action in quantitative trace analysis is perhaps more important than in the corresponding qualitative investigations. This is the reason that the first studies on collector action dealt with quantitative methods of determination. H. N. Stokes and J. R. Cain [*J. Am. Chem. Soc.* **29**, 427 (1907)] were the first to show that traces of $Fe(OH)_3$ can be collected by means of MnO_2, and traces of FeS by CdS. Shortly thereafter G. Bertrand and M. Javillier [*Bull. soc. chim.* [4] **3**, 114 (1908)] showed that, if zinc salt solutions are warmed with milk of lime, exceedingly small quantities of zinc are retained as calcium zincate by the CaO particles. The zinc can be localized in this way from a solution as dilute as 1:30,000,-000 and thus made accessible to quantitative determination. E. B. Sandell in his Colorimetric Determination of Traces of Metals, Interscience Publ. Co., New York, 1944, has described the quite varied applications of the collector action of induced precipitations in quantitative trace analysis.

Rajmann[197] found that, if zirconium and titanium are both present, almost all of the titanium is coprecipitated on precipitation with arsenate. The titanium can then be detected by the hydrogen peroxide reaction, after centrifuging and dissolving the precipitate in sulfuric acid. The titanium can still be detected easily in 10 ml. of a solution that contains titanium in the ratio of 1:10,000,000, by adding one drop of 1% zirconium solution and precipitating with twenty drops of 20% arsenic acid, centrifuging, and applying the pertitanate reaction. This accumulation procedure can be used advantageously for the detection of small amounts of titanium in the presence of large amounts of iron, vanadium, and chromium, namely, under conditions at which the normal hydrogen peroxide test fails. Chuiko[198] found that aluminum hydroxide, precipitated by ammonia or alkali carbonate, acts as a collector for $Ti(OH)_4$, provided iron or other metal ions, precipitable by ammonia, are absent. After dissolving the mixed hydroxides, traces of titanium (of the order of 1γ Ti/1000 ml.) can be detected. Blumenthal[199] made the interesting observation that a precipitate of MnO_2, produced by reaction of Mn^{++} and MnO_4^- ions will completely remove antimony, tin, or bismuth from sulfuric or nitric acid solutions. A procedure based on this collector action of MnO_2 has been improved by Kallmann and Pristera[200] for the determination of small amounts of antimony in copper alloys, and extended to the determination of small amounts of antimony, tin, and bismuth in metals, alloys, and ores. Since the salts of these metals derived from mineral acids hydrolyze very extensively, it is probable that the collector action of MnO_2 is due to its adsorption of the hydrolysis products of the antimony, tin, and bismuth salts. An analogous action toward titanium and zirconium salts may be expected. It should be noted that MnO_2, in an alkaline medium, is an excellent collector for traces of $Fe(OH)_3$ (see Chapters X and XI concerning trace gathering). Other examples of induced precipitations follow.

Zinc salts react with alkali mercury thiocyanates to form the complex $Zn[Hg(CNS)_4]$, which comes down as a heavy, white crystalline precipitate. Ferric salts give no precipitate with $[Hg(CNS)_4]^{--}$ ion, but produce a red coloration due to the formation of soluble ferric thiocyanate complexes. When zinc salts contain ferric iron, the addition of $K_2[Hg(CNS)_4]$ produces a pink to red precipitate.[201] If the quantity of iron is considerable, the precipitate is deep red-violet and retains this

[197] F. Feigl and E. Rajmann, *Mikrochemie* **19**, 60 (1935).

[198] V. T. Chuiko, *Chem. Abstracts* **34**, 1783 (1940).

[199] H. Blumenthal, *Z. anal. Chem.* **74**, 33 (1928).

[200] S. Kallmann and F. Pristera, *Ind. Eng. Chem., Anal. Ed.* **13**, 8 (1941).

[201] F. Feigl, *Spot Tests*, p. 140.

color even after thorough washing with hot water.[202] These precipitates contain so little iron that a stoichiometric compound of zinc-iron mercuric thiocyanate is out of the question. Nevertheless, the tinting of $Zn[Hg(CNS)_4]$ through the presence of ferric·salts raises the sensitivity of the zinc test considerably, since a colored precipitate can always be perceived more readily than a colorless one, particularly when smaller quantities are involved. The formation of the colored zinc mercuric thiocyanate, due to the coprecipitated ferric compound, obviously involves a phenomenon quite similar to that encountered in the simultaneous formation of $Zn[Hg(CNS)_4]$ and $Cu[Hg(CNS)_4]$. In this latter case, the precipitate does not have the mixed color of the white zinc salt and the yellow-green copper salt,[203] but instead a violet material is formed. It is possible to detect small quantities of zinc or of copper[204] by this effect. According to Straumanis and Ence,[205] the system $Zn[Hg(CNS)_4] - Cu[Hg(CNS)_4]$ does not involve the production of a compound, but rather the formation of mixed crystals. A quite important induced action occurs when zinc is precipitated with $[Hg(CNS)_4]^{--}$ in the presence of excess nickel salts. A yellow-green precipitate is formed immediately.[206] Its composition approximates $4Zn[Hg(CNS)_4]·Ni[Hg(CNS)_4]$. The induction action in this case obviously is connected with the formation of a chemical compound, since nickel salts, when alone, react with $K_2[Hg(CNS)_4]$ only in concentrated solutions, and then produce not more than a slight precipitate, even after long standing. According to Korenmann,[207] cobalt salts act like the nickel salts. Consequently, the test for cobalt with alkali mercuric thiocyanate based on the formation of blue crystalline $Co[Hg(CNS)_4]$, becomes much more delicate if $Zn[Hg(CNS)_4]$ is formed simultaneously, even in large quantity. Krumholz and Sanchez[208] found that cobalt and zinc solutions, so dilute that singly they no longer react with mercuric thiocyanate, immediately give à blue precipitate if they are together. In most of the precipitations induced by the formation of $Zn[Hg(CNS)_4]$, the condition under which the zinc compound is formed is of decisive importance. This is shown by experiments using previously prepared $Zn[Hg(CNS)_4]$. If such material is shaken or even warmed with copper, ferric, or ferrous salts in the presence of $K_2[Hg(CNS)_4]$, the white zinc salt is not tinted.

[202] F. FEIGL, Studies with L. Weidenfeld. Dissertation, Vienna, 1930.

[203] R. MONTEQUI, Chem. Abstracts 21, 2858 (1927).

[204] F. FEIGL, Mikrochemie 7, 6 (1929).

[205] M. STRAUMANIS and E. ENCE, Z. anorg. allgem. Chem. 228, 334 (1936).

[206] L. WEIDENFELD, Dissertation, Vienna, 1930; compare also J. KORENMANN, Z. anal. Chem. 95, 44 (1933).

[207] J. KORENMANN, loc. cit.

[208] P. KRUMHOLZ and J. SANCHEZ, Mikrochemie 15, 114 (1934).

An instructive instance of the improvement of a test through induced precipitation is provided by $BaSO_4$-$PbSO_4$ if precipitated under special conditions. The addition of sulfuric acid produces no precipitate from lead solutions containing much alkali acetate. Clear solutions can be prepared in this way, as well as by the addition of alkali acetates and acetic acid to lead sulfate. If these solutions, which contain undissociated lead acetate (see Chapter IV) are used instead of sulfuric acid or sodium sulfate as precipitant for barium, considerable quantities of lead sulfate coprecipitate with the barium sulfate.[209] The ordinary test for barium can thus be made about eight times as sensitive as usual.[210] It has not yet been determined whether this induced reaction involves the formation of a double sulfate, or the production of mixed crystals, or an adsorption complex that cannot be formulated stoichiometrically. Changes of properties in materials adsorbed on barium sulfate or coprecipitated with it were pointed out on p. 148. The observations of Wohlers[211] are very interesting in this regard. He found that permanganates, thiocyanates, or ferric salts adsorbed on barium sulfate have lost completely their usual ability to react with hydrogen peroxide, sulfurous acid, ferric salt, or thiocyanate. This effect is most plainly shown by barium sulfate that has been precipitated in the presence of much $KMnO_4$. The $BaSO_4$ precipitate is violet, and the color is not lightened appreciably by treatment with sulfur dioxide, oxalic acid, tartaric acid, or hydrogen peroxide. Feigl and Aufrecht[212] have used this tinting for the detection of small amounts of barium or sulfate. Yagoda[213] refined the procedure and showed that as little as 2γ Ba, at a dilution of $1:1,000,-000$, can be determined colorimetrically by means of this tinted precipitate. He also showed that $BaSO_4$ is not colored if it is precipitated by sodium sulfate in the presence of $NaMnO_4$. Likewise, little effect is produced by ammonium sulfate, sulfuric acid, cesium sulfate, and other sulfates in solutions containing no potassium ions. Presumably the latter must be present to introduce the chromogenic MnO_4^- ion into the $BaSO_4$ crystal lattice. This case of induced precipitation doubtless involves the formation of mixed crystals, a consequence of the fact that the ionic radii of potassium and barium are almost identical (1.33Å and 1.35Å, respectively).[214]

[209] F. FEIGL, Experiments with J. Tamchyna and L. Weidenfeld; compare F. FEIGL, Z. angew. Chem. **43**, 550 (1930).

[210] F. FEIGL, Spot Tests, p. 167.

[211] H. WOHLERS, Z. anorg. allgem. Chem. **59**, 203 (1908).

[212] F. FEIGL and W. AUFRECHT, Rec. trav. chim. **58**, 1127 (1939).

[213] H. YAGODA, J. Ind. Hyg. Toxicol. **26**, 224 (1944).

[214] An analogous effect may be involved in the findings of I. M. KORENMANN [Chem. Abstracts **31**, 7001 (1937)]. He observed that $RbClO_4$ and Ag_2SO_4 are highly

Among the induced precipitations that can be used in gravimetric analysis is the quantitative precipitation of molybdenum sulfide from acid solutions when accompanied by the production of nascent sulfur. Hydrogen sulfide precipitates molybdenum ·sulfide incompletely from acid molybdate solutions; a quantitative precipitation can be accomplished only when the gas acts under pressure. However, if hydrogen sulfide is passed into an acidified molybdate solution and some potassium iodide-iodine solution introduced at the same time, free sulfur is formed and this leads to the complete precipitation of the molybdenum, perhaps as a polysulfide.[215] A very remarkable method for the completion of a sulfide precipitation through simultaneous formation of another sulfide has been described by Gaze.[216] Hydrogen sulfide precipitates black PtS_2 incompletely from platinic solutions, because the platinum in hydrochloric acid solution is present almost solely as the complex anion $[PtCl_6]^{--}$. It therefore is accessible to the action of H_2S only so far as the dissociation $[PtCl_6]^{--} \rightleftharpoons PtCl_4 + 2Cl^-$ permits. However, platinic sulfide is precipitated quickly and completely if 5 to 10% of mercuric chloride or nitrate solution is added. Accordingly, a shift of the equilibrium position of the foregoing reaction is connected with the simultaneous formation of mercuric sulfide. In addition, the coprecipitated HgS makes the PtS_2 precipitate easier to filter. The mercury sulfide is easily removed by igniting the precipitate and hence this method of precipitating platinum can be used for its quantitative determination.

Coprecipitation can not only make incomplete sulfide precipitations quantitative, but instances are known in which traces of metal sulfides, whose precipitation, when alone, is so slight as to be invisible, are incorporated by coprecipitation in another sulfide. An example is the precipitation of traces of PbS by coprecipitation with HgS. This procedure is recommended by Scott.[217] Feigl and Braile[218] proved that this trace-catching precipitation of HgS, combined with the detection of lead by the sensitive rhodizonate reaction (see p. 175), makes it possible

colored if they are precipitated in the presence of $KMnO_4$. He used this effect as a test for permanganate.

[215] F. FEIGL, *Z. anal. Chem.* **65**, 25 (1924). A granular precipitate of ZnS that filters well can be obtained in this way. R. BORNEMANN [*Z. anorg. allgem. chem.* **82**, 216 (1913)] was the first to observe that ZnS, which normally is gelatinous, can be obtained in a dense form that filters well, by coprecipitating sulfur with it. He recommends passing H_2S into a zinc solution that contains acetic or chloroacetic acid together with $NaHSO_3$.

[216] R. GAZE, *Apoth. Ztg.* **27**, 959 (1912); *Chem. Abstracts* **7**, 577 (1913).

[217] W. W. SCOTT, Standard Methods of Chemical Analysis, 5th Ed., p. 514. New York, 1939.

[218] F. FEIGL and W. BRAILE, *Analyst* **69**, 147 (1944).

to detect lead in 100 ml. of water, even at a dilution of 1:100,000,000. It is remarkable that HgS by no means acts as collector for all metal ions that form precipitable sulfides. Its behavior is selective. For example, the action of HgS toward coprecipitated CuS and Ag_2S is much less than toward PbS.[219] There seems to be a connection here between co- and post-precipitation as stated on p. 153. Reference[220] will only be made to the activity of CuS as a trace catcher for the sulfides of zinc, lead, and molybdenum. A record example of the collector action of a sulfide precipitation was furnished by Stock and his coworkers.[221] They found that as little as 0.02γ Hg can be collected from 500 ml. of solution, by coprecipitation of CuS. This corresponds to the enormous dilution of 1:2,500,000,000.

An induced precipitation with collector action resulting from a redox reaction was described by Kuehnel-Hagen.[222] It has considerable analytical interest. He found that the deposition of free tellurium (from sodium tellurite by the action of sulfur dioxide or stannous chloride) causes a quantitative coprecipitation of small quantities of platinum (also of gold, molybdenum, or mercury). It is thus possible to separate and detect very small amounts (less than 0.0001%) of admixed platinum. Probably traces of this metal, which *per se* are not visible, serve as nuclei for the tellurium precipitate, and thus are carried down with it. It is also possible that nascent tellurium converts the traces of metal into telluride, which is then carried down with the free tellurium. This instance again emphasizes the wide variety of the mechanisms of induced precipitations. Many of these have not been completely clarified as yet.

In all the preceding examples, the products of the inducing and of the induced precipitation were entirely inorganic. This limitation, however, is not general. Strock and Drexler[223] showed that small quantities of zirconium, titanium, and vanadium are coprecipitated when ferric iron is brought down with cupferron (see p. 262). Scott and Mitchell[224]

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[219] B. E. COHN [*Chemist Analyst* **29**, 63 (1940)] showed that the hindering (masking) of the precipitation of PbS from a solution containing fluoborate ions is destroyed by adding $HgCl_2$. All the lead is then brought down, along with the HgS, by H_2S. This observation indicates that the PbS precipitation is not due simply to demasking (see Chapter IV), but rather that the deposition of HgS produces a sulfidic lead compound which has a lower solubility product than PbS. Possibly a mixed sulfide with the formula $Pb[HgS_2]$ is formed.

[220] R. E. LUTZ, *J. Ind. Hyg. Toxicol.* **7**, 273 (1925); A. LUCAS, *Mikrochemie*, Emich Festschrift, p. 199 (1930); A. v. HEVESY, *Z. anorg. allgem. Chem.* **214**, 380 (1933).

[221] A. STOCK, H. LUX, F. CUCUEL and H. KÖHLE, *Z. angew. Chem.* **46**, 62 (1933).

[222] S. KUEHNEL-HAGEN, *Mikrochemie* **20**, 182 (1936).

[223] L. W. STROCK and S. DREXLER, *Chem. Abstracts* **35**, 3166 (1941).

[224] R. O. SCOTT and R. MITCHELL, *J. Soc. Chem. Ind.* **62**, 5 (1943).

found that iron or aluminum precipitated with oxine (see p. 183) acts as collector for small amounts of cobalt oxinate. The induced precipitation by organic reagents deserves consideration in trace analysis, because these reagents *per se* often have a selective action, and because metalloorganic compounds can subsequently be converted by ignition into oxide or carbonate, which lend themselves well to identification tests.

The analytical importance of induced precipitations resides in the fact that they are frequently related to, or can be brought into relation with, the particularly pertinent problems of unequivocality and sensitivity of test reactions. All the known examples of induced precipitation exhibit, under certain circumstances, a decided limitation of their action to particular cosolutes. This selectivity is chargeable (see p. 164) to various causes. In addition to those already mentioned, it will be merely pointed out that some induced precipitations can be regarded as topochemical reactions (see Chapter XI). Cognizance of the possible occurrence of induced precipitations is important in avoiding errors that may arise in the course of analytical operations because of these anomalous precipitations. More significant, however, is the possibility of using the fact that small quantities of material may bring about induced precipitations, and therefore minimal quantities often can be collected from very dilute solutions by an induced precipitation and thus be made accessible to an identification test. It may be expected that the discovery, employment, and also the avoidance of induced precipitations may lead to improvements in analytical procedures. In qualitative analysis, the utilization of induced precipitation is in harmony with the author's creed that all possibilities should be considered if there is any chance that they may lead to sensitive and unequivocal tests. The possible employment of induced solubility likewise belongs in this category. However, the only available example is that of the solubilization of anhydrous $CrCl_3$ (see p. 156). No attention has been given as yet to the use of induced precipitations in qualitative organic analysis. However, the striking success of chromatographic analyses (see Chapter X) in which traces of organic compounds are retained by suitable adsorbents, makes it quite likely that induced precipitations are possible in qualitative organic analysis also, and will eventually be employed in this field.

The Effect of Certain Atomic Groupings on the Specific and Selective Activity of Compounds in Inorganic Analysis

Organic compounds are winning an increasingly important place as reagents in inorganic analysis because their application often leads to precipitations and color reactions which possess far greater sensitivity and limitation of action than are displayed by reactions with inorganic reagents.[1] It is not possible at present to make definite predictions as to which of the many organic compounds are suitable for analytical purposes, and, for the most part, it is still necessary to rely on empirical trials. However, certain principles of classification (according to the structure of the reaction products), and several rules (with regard to the ascription of certain effects to definite atomic groups), make it possible to proceed methodically when searching for new organic reagents and when trying to improve certain types of organic reagents that are already in use.[2]

The ability to form salts is of prime importance in the case of organic compounds to be used as reagents. Such salt formation is primarily due to the presence or development of certain acidic or basic groupings. The following groups fall into this category:

Carboxyl
$$-C\overset{\displaystyle O}{\underset{}{\parallel}}-OH$$

Sulfonic
$$-S\overset{\displaystyle O}{\underset{\diagdown OH}{\parallel}}=O$$

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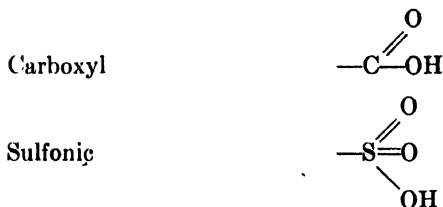
[1] An excellent and exhaustive description of organic reagents can be found in F. J. WELCHER, Organic Analytical Reagents, 4 vol., Van Nostrand, N. Y., 1947–48. A good survey, up to 1941, of the recommended organic reagents is given in J. H. YOE and L. A. SARVER, Organic Analytical Reagents, N. Y., 1941. Other books dealing with the subject are: The Staff of Hopkin and Williams, Organic Reagents of Metals, 3rd ed., London, 1938; The Staff of Hopkin and Williams, Organic Reagents for Organic Analysis, Brooklyn, 1946; I. MELLAN, Organic Reagents in Inorganic Analysis, Philadelphia, 1941; P. VON STEIN, Organic Reagents in Inorganic Analysis, Brooklyn, 1942; International Committee on New Analytical Reagents, Table of Reagents for Inorganic Analysis, Leipzig, 1938; Reactifs pour l'analyse Qualitative Minerale recommendés par la Comité Internationale—Deuxieme Rapport. Edited by P. WENGER and R. DUCKERT, Basle, 1945; J. F. FLAGG, The Use of Organic Reagents in Gravimetric and Volumetric Analysis, New York, 1948; W. PRODINGER (see note 5).

[2] Compare F. FEIGL, *Ind. Eng. Chem., Anal. Ed.* **8**, 401 (1936).

Sulfinic	$-S\overset{O}{\underset{OH}{\big<}} \rightleftharpoons -S\overset{O}{\underset{O}{\big<}}H$
Arsonic[2a]	$-As\overset{OH}{\underset{OH}{=O}}$
Oximic	$=N-OH \rightleftharpoons =N\overset{O}{\diagup}H$
Nitro (primary)	$-CH_2-NO_2 \rightleftharpoons -CH=N\overset{OH}{=O}$
Nitro (secondary)	$R\overset{\mid}{C}H-NO_2 \rightleftharpoons R\overset{\mid}{C}=N\overset{OH}{=O}$
Enolic	$\diagdown\!\!\underset{\diagup}{C}-CH_2-C\overset{O}{\diagdown} \rightleftharpoons \diagdown\!\!\underset{\diagup}{C}-CH=C\overset{OH}{\diagdown}$
Phenolic (alcoholic)	$\diagdown\!\!\underset{/\!/}{C}-OH$
Thiophenolic	$\diagdown\!\!\underset{/\!/}{C}-SH$
Thioenolic	$\diagdown\!\!\underset{\diagup}{C}=\overset{\mid}{C}-SH \text{ or } -N=\overset{\mid}{C}-SH$
Sulfonamidic	$-S\overset{O}{\underset{O}{\big<}}NH_2 \rightleftharpoons -S\overset{O}{\underset{NH}{\big<}}OH$
Acid-imide	$-CO-NH-CH_2$
Basic groups that are derivatives of ammonia	$-NH_2$; $-NHR$; $-NR_1R_2$; and cyclically bound nitrogen atoms

Experience has shown that the use of organic reagents of an acidic nature and having specific or selective action almost always involves formation of inner complex compounds (see Chap. III). Inspection of its structural formula will disclose whether an acidic organic compound has this capability. The formation of inner complex salts presupposes the presence of one of the acidic groups just listed along with atoms capable of developing auxiliary valences and situated in such proximity to acidic hydrogen atoms that a ring-closure (5- or 6-membered) is possible through the action of principal and auxiliary valences. In the

[2a] Note should be taken also of ester acids of arsenic and phosphoric acid. Concerning the latter see p. 294.

production of inner complex salts, attention should, as a rule, be directed to the presence of oxygen, sulfur, or nitrogen atoms in the following groups: —CO, —CS, —NH$_2$, —NHR, —NR$_1$R$_2$, —NO, —NO$_2$, as well as to the nitrogen atoms or double-bonded carbon compounds in open or closed chains.[3]

It is necessary to keep in mind not only the formation of normal and inner complex salts, but also the fact that molecules of certain neutral or basic organic compounds can be joined to inorganic molecules or ions through the action of auxiliary valences. Mixed inorganic or organic compounds, which may be electrolytes or non-electrolytes, result. Furthermore, the activity of auxiliary valences may link molecules of acidic organic compounds (especially carboxylic acids or oximes) to metal acids or their anhydrides, with production of heteropolyacids (see Chapter III. The chemical adsorption of certain dyestuffs by metal oxides and hydroxides or, in general, the formation of adsorption complexes or compounds that play a part in color lake reactions (see Chapter X) can also be ascribed to the activity of auxiliary valences. The direct ncorporation of parts of an inorganic compound that has no salt character is rare, although some examples are known.[4] Instances of the participation of inorganic compounds in the transformation of organic compounds by oxidation or reduction actions are more common.

In the types of compounds cited there is always a dependence on the presence and the position of certain groups. Such relationships can be recognized and used accordingly, notably in the formation of normal and inner complex salts, as well as in the coordination of organic compounds on inorganic components. If salt-forming organic reagents are considered, for example, the presence of one of the acidic or basic groups listed is, of course, indispensable. However, other atoms or groups contained in the molecule sometimes exert a fundamental effect both on the specificity or selectivity of the salt formation, as well as on the color and solubility of the salts being considered (compare Chapters VIII and IX). This circumstance is, consequently, important, because organic compounds can undergo extensive alterations in their structure as a result of condensation and substitution reactions, with sufficient resulting modification of the properties of the salts that they can then be used for analytical purposes. It is of great importance in the search for new organic reagents and their analytical application, and in the improvement of the effectiveness of those already in use, that certain groups in organic compounds frequently have a very definite effect on the solubility, color,

[3] Compare H. M. HAENDLER and B. T. GEYER, *J. Am. Chem. Soc.* **60**, 2813 (1938), regarding a classification of chelate groups in organic compounds.

[4] F. FEIGL, Spot Tests, pp. 196, 261.

etc., of salts.   Pertinent examples will be given that are of importance both for special practical cases and for the chemistry of selective and specific reactions in general.

The discussion of the examples of specific and selective group actions to be described presently can be appropriately preceded by several remarks of fundamental importance to the understanding of the activity of organic reagents, and to the intelligent pursuance of comprehensive investigations in this field.   It can be unquestionably established in many cases that the color and solubility of the reaction products of organic reagents are dependent on the presence of quite definite atomic groups.   Such groups can, therefore, properly be designated as metal-binding groups, or as groups with specific or selective action.   However, it must not be forgotten that the prevailing reaction conditions may also exert an important influence on all chemical reactions.   This is particularly true when organic reactants are involved.   Such effects can be so far-reaching that a specific or selective action of a group sometimes is actually determined by the reaction conditions.   The considerable number of factors that can influence a specific or selective group action will be briefly indicated.   In the first place, both, or at least one, of the reactants should be in solution, so that the reactions involved in the analysis will proceed rapidly.   Consequently, solubility in water is always a desirable property of an organic reagent.   Furthermore, the solubility of reaction products in water, or in organic reagents, plays a dominant role in the attainment of specific and selective actions, as well as in determining the sensitivity of a test.   Hence, the proper choice of solvents and close attention to the factors which affect the solubility of compounds are important (see Chapters VIII and IX).   The fact that numerous organic reagents are active solely in alkaline solution is directly connected with solubility.   This is the case when, through the action of OH^- ions, organic compounds undergo a rearrangement so that a neutral group is converted into a salt-forming (*aci*) group, or when the reagent is a weak acid whose solubility in water is too slight to enable it to deliver a sufficient concentration of active anions.   In both cases, the addition of alkali brings about the formation of water-soluble alkali salts.   Only then will the anion concentration be adequate to attain the particular ion concentration so that an analytically valuable reaction may take place. Sometimes the solution of an organic reagent in organic solvents may present an aci-baso equilibrium, in which the concentration of the salt-producing form is sufficient to react with only one ionic species.   In such cases, there is a specific action, whereas the same reagent at a greater concentration of the aci-form (*e.g.*, on addition of OH^- ions) can become completely non-specific in its action.   Besides the extreme instances just

mentioned, the reaction products of organic reagents often exhibit a gradation in their resistance toward certain pH values. If this is true over sufficiently wide ranges, a reagent may develop a specific or selective action, provided a certain pH is maintained, whereas neglect of this detail may result in either no reaction or, at most, in a non-specific one. It is also important to note that products of organic reagents, though produced in an alkaline medium, are occasionally stable toward acids, even though the particular compound cannot be formed in acid solution. This phenomenon, in well marked form, is encountered with purely inorganic compounds only in the cases of cobalt and nickel sulfide. It is often encountered among inner complex salts and, obviously, a test may sometimes be made specific or selective by taking advantage of this effect. Organic reagents, by virtue of certain of their groups, are sometimes endowed with the ability to form salts directly, as well as through mere addition of the whole molecule. This ability may lead to an entirely different type of reaction with the same reagent; an effect which may be useful in analysis. Another factor of great importance is that the selective action of an organic reagent can often be increased by masking of cosolutes showing similar reactions (see Chapter IV). At times this enhancement actually leads to specificity. Finally, in considering the factors affecting the activities of organic reagents, it must not be forgotten that oxidizing or reducing compounds may sometimes cause a decomposition of the reagent with the result that a group action is destroyed.

If the multiplicity and variety of factors that·may play a part in the application of organic reagents is seriously considered, it becomes apparent that *it is never proper to speak of the specific or selective action of atomic groups independently of the reaction conditions.* Rather, the action of atomic groupings is always a direct function of definite reaction conditions. This statement signifies that the presence of certain atomic groups is a necessary, but not always a sufficient, condition for specific or selective actions. Therefore, it is better not to speak of specific or selective reagents, but rather of specific or selective reactions, or it is still more correct, to refer to specific or selective tests, because even though not stated, the importance of the reaction medium is then tacitly included.[5]

[5] W. PRODINGER'S Organic Reagents Used in Quantitative Inorganic Analysis (translated by S. Holmes), Elsevier Publishing Company, New York, 1940, is a useful compilation of the findings and methods developed by others. Prodinger believes that he has made a contribution of his own by introducing (p. 117) the term "non-specificity." He defines this "as the number of elements or element groups which may also react with the reagent under the reaction conditions and disturb the test. For example, if under the determination conditions, there are two other elements in

Another point of fundamental importance should be stressed here. Under the given experimental conditions, the specific or selective action of organic reagents frequently is paralleled by a specific or selective salt-formation. However, this is not necessarily always true. Instances are known in which a reagent forms a colored soluble compound with one ionic species, and colorless soluble or colorless insoluble products with other ionic species. Furthermore, examples can be cited to show that a reagent can react with various ions to produce insoluble compounds differing characteristically from each other in color. Hence, it is entirely proper to refer to such reagents (reactions) as specific or selective, insofar as analytical use is made of such differences. Accordingly, specificity and selectivity will be considered primarily in the sense of analytical applicability, rather than with reference to a specific or selective capacity for forming salts.[6]

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addition to the one sought, which may also react, then the test has a non-specificity of 2. A specific reaction, therefore, has a non-specificity of 0." The author believes this proposed term to be utterly valueless. In the first place, it seems meaningless to state that a specific test has a non-specificity of 0, and to say of a selective test that a non-specificity exists. However, the real objections to this unfortunate concept are of greater moment. Prodinger has overlooked the fact that instances can be brought forward which demonstrate that a particular cosolute can interfere with a test to quite different degrees, even though the other conditions are identical. The extent of the effect is often dependent on the quantity of cosolute present. Therefore, it is important to know the limiting proportions both in qualitative and quantitative procedures. Sometimes, a reaction, though carried out under the same conditions, exhibits a quite different selectivity when employed in qualitative tests rather than in quantitative determinations. Furthermore, two materials, which singly do not interfere with a test, sometimes produce marked interference if both are present. The extent of the impairment often depends on the relative amounts present. Consequently, the possibilities are far too varied and numerous to attach much concrete significance to numerical values of specificity. A mere enumeration of interfering cosolutes serves no purpose; it is essential to know what materials are involved and at what limiting proportions interferences can occur.

[6] The question as to who is the real originator of an organic reagent is one which is often debated. Is it the one who first demonstrated the characteristic salt-forming ability, or is it he who first made analytical use of a previously known salt-forming ability? As a rule, the two workers were attempting to solve different problems, and, since analytical application is the predominant criterion in this book, it is logical to award the credit to the investigator responsible for the actual advance in analytical chemistry. A reasonable doubt can only arise if a very short interval separated the demonstration of a characteristic salt formation and the proof that it could be used in analysis. This happened in the case of dimethylglyoxime when Ni-reactivity was discovered by Tschugaeff in 1905, and was introduced in analysis two years later by Brunck, as a reagent for nickel. Actually, the latter was preceded by K. KRAUT [Z. angew. Chem. 19, 1793 (1906)]. As a rule, years or even decades intervene between

The fact, as will be demonstrated presently, that specific and selective actions of organic reagents are assuredly related to the presence of certain atomic groupings in the reagent is not merely important to the discovery, development, and improvement of identifying tests and methods of quantitative determination of metals and compounds in inorganic analysis. The principle of group action plays an important role also in qualitative organic analysis. This will be discussed in Chapter VII.

Acidic OH Groups Bound to Carbon Atoms

Experience has shown that phenolic OH groups are particularly prone to take part in specific and selective formations of salts involving OH groups bound to carbon atoms. In aliphatic compounds, alcoholic OH groups adjacent to carbon double bonds are active. Enolic OH groups produced by the shift of an adjacent hydrogen atom in ketones, or formed from the keto-oxygen atom: $\diagdown C{=}O \rightarrow \diagdown C{-}OH$, also belong in this category. This group quite generally exhibits much more similarity to phenolic OH groups than to the OH groups of primary, secondary, or tertiary alcohols. It appears, however, that the acidic character of a single phenolic or enolic OH group in the molecule of an organic compound is not of itself sufficient to cause the formation of insoluble or characteristically colored soluble heavy metal salts. This also holds for the OH groups in the carboxyl groups of acids. Analytically interesting solubility and color effects accompanying salt formation involving OH groups bound to C atoms, as a rule, only appear if a second acidic group, which is likewise salifiable, is adjacent to the OH group, or if an adjacent group offers the possibility of an auxiliary valence binding. Under such circumstances, a metal atom can become part of a 5- or 6-membered ring through the action of two principal valences, or of one principal and one auxiliary valence. Such ring formations and the dependence of the ring stability on definite pH values can often be brought into direct relation to the selective actions of the particular parent acidic organic compounds.

This section will deal with the action of OH groups that produce salts which are the basis of selective color and precipitation reactions. Consequently, the discussion here will not include references to the selective actions of OH groups in aliphatic or aromatic compounds which can function as masking agents (compare Chapter IV).

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the two stages, so that there is ordinarily little doubt as to the accredited originator in the case of most of the modern organic reagents.

The Specific and Selective Action of Rhodizonic Acid

The analytical use of the formation of insoluble salts of rhodizonic acid is comparatively recent.[7] Nevertheless, the discussion of the behavior of this material as a reagent is placed first because important relations between reaction conditions and specific or selective action of atomic groups are exhibited by this compound.

Rhodizonic acid (I) can be used only in the form of its alkali salts. Although they are green-black solids, their aqueous solutions are deep to light orange, depending on the concentration. The color disappears completely if the solution is acidified, and returns on the addition of sufficient alkali. This color change indicates that the alkali salts of rhodizonic acid have a constitution different from that of the free acid. Solutions of sodium rhodizonate probably contain some of the undissociated salt in which the metal is bound through auxiliary valences to the neighboring oxygen atoms of the CO groups. Accordingly, the sodium salt, for instance, would be written as an inner complex salt, as shown in (II):

(I) (II)
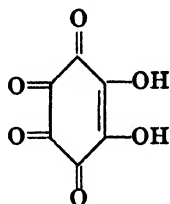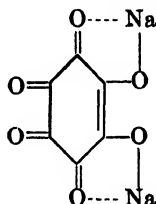
This formulation of sodium rhodizonate as an inner complex salt is supported not only by its color, but also by its solubility, which is strikingly low for an alkali salt (0.2 g./100 ml. water). The potassium salt is even less soluble.

Solutions of alkali rhodizonates exhibit a behavior toward metal ions that has considerable interest from the analytical standpoint since the action is limited to certain uni- and divalent metals. Intensely colored salts of rhodizonic acid are invariably formed insofar as precipitation and not reduction reactions occur. This finding indicates the probable production of inner complex salts, whose constitutions are analogous to that just ascribed to sodium rhodizonate. The following table sum-

[7] F. Feigl [*Mikrochemie* **2**, 188 (1924)] was the first to recommend sodium rhodizonate as a spot test reagent for barium and strontium. This paper led to numerous studies by other workers on the analytical use of sodium rhodizonate. A survey of the literature, together with a description of a specific test for lead, is given by F. Feigl and H. A. Suter, *Ind. Eng. Chem., Anal. Ed.* **14**, 840 (1942).

marizes the results obtained with 1% neutral and acidified metal salt solutions, and with the corresponding metal hydroxides and oxides:

TABLE I

Action of Sodium Rhodizonate

Metal ion	Metal salt solution (neutral)	Metal salt solution (pH = 2.8)	Hydroxide	Oxide
Silver........	Black ppt.[a]	Black ppt.[a]		
Mercury (I)..	Brown-red ppt.	Brown-red ppt.		
Thallium. ...	Dark brown ppt.	Brown-black ppt.		
Lead.. .	Blue-violet ppt.	Scarlet-red ppt.	Blue-violet	Blue-violet
Copper.....	Orange-red ppt.			
Mercury (II).	Orange-yellow ppt.[b]			
Cadmium. .	Brown-red ppt.	Brown-red ppt.	Gray-brown	
Bismuth.....	Brown-red ppt.	... .	Brown-red	
Tin (II)... ..	. ...	Violet ppt. [c]	Violet	
Tin (IV).....				
Nickel.. ..				
Cobalt.. ..				
Iron (II). .	Red-brown ppt.			
Iron (III) . .	Blue-green color[c]	Blue-green color[c]		
Zinc.. ..	Brown-violet ppt.	. .. . ..	Brown-violet	Brown-violet
Manganese .				
Uranyl.. . .	Brown ppt.		'	
Aluminum...				
Beryllium. ..				
Magnesium				
Calcium.....	. . . ..	. .	Brown-red	Brown-red
Strontium. .	Red-brown ppt.	. . .. .	Red-brown	Red-brown
Barium..	Red-brown ppt.	Red-brown ppt.	Red-brown	Red-brown
Zirconium....				

[a] Silver reduction.   [b] Chiefly calomel.   [c] Phenol reaction.

Inspection of these findings shows that the action of sodium rhodizonate on neutral solutions, as well as on oxides and hydroxides, extends over numerous uni- and divalent metal ions (or their oxides and hydroxides). Bi^{+++} probably functions as the BiO^+ ion. At pH = 2.8, the activity is markedly more limited, and therefore more selective. Copious precipitation is obtained only with Pb^{++}, Sn^{++}, Bi^{+++}, Ba^{++}, and Sr^{++} ions.

The lead salt is the least soluble of all the metal rhodizonates; hence, an extremely sensitive lead test has been developed on this basis. The solubility of this salt is so slight that even such "insoluble" materials as lead sulfide, sulfate, *etc.*, react with sodium rhodizonate. It is easy to separate lead from other metal ions by precipitating it with sulfuric acid,

and since barium sulfate does not react with sodium rhodizonate, a specific test for lead is provided by sodium rhodizonate or rhodizonic acid. The red precipitate formed at pH = 2.8 corresponds to the formula $2PbC_6O_6 \cdot Pb(OH)_2 \cdot H_2O$. A more basic salt, $PbC_6O_6 \cdot Pb(OH)_2 \cdot H_2O$, is obtained from neutral solutions; it is violet. The black thallium salt has the composition $Tl_2C_6O_6$.

The following compilation shows how interesting and analytically useful is the selective activity of sodium rhodizonate within the alkaline earth group. Positive response is given by:

<div style="margin-left:3em">

Ba, Sr, Ca (as hydroxides)
Ba   (as carbonate)
Ba, Sr   (in neutral solution)
Ba   (in weakly acid solution)

</div>

Hence the action of this $O{=}C{-}C{-}OH$ group toward alkaline earth

$$O{=}C{-}C{-}OH$$
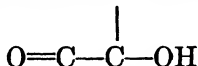
metals shows a characteristic gradation. This corresponds to the regularities that are often encountered elsewhere in the behavior of oxides and salts of the alkaline earths with the same anion.[8]

A comparison of the formulas of rhodizonic acid and tetrahydroxyquinone
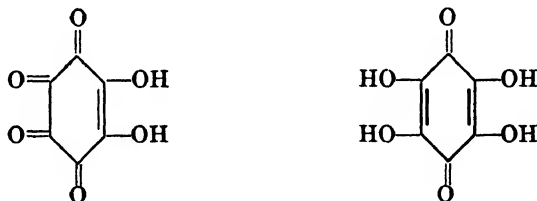
shows that both compounds contain a similar grouping of OH— and adjacent coordinatable CO groups. In fact, Gutzeit[9] has shown that the reactions of tetrahydroxyquinone are quite analogous to those of rhodizonic acid.

The behavior of sodium rhodizonate with acetic acid solutions of organic bases has been studied and seems to be interesting. Benzidine, which, because of the slight solubility of its sulfate, can, to a certain extent, be regarded as an organic counterpart of barium and lead ions, produces a crystalline violet rhodizonate precipitate in dilute solutions. Less sensitive reactions are given by other aromatic primary amines, and also benzylamine, which, without exception, form colored precipi-

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[8] In all likelihood, radium rhodizonate will be found to be more acid-resistant than barium rhodizonate.

[9] G. GUTZEIT, *Helv. Chim. Acta* 12, 713, 829 (1929).

tates. Preliminary trials have shown that secondary and tertiary amines, as well as hydrazine, hydroxylamine, and phenylhydrazine, are inactive. The colored amine salts of rhodizonic acid can also be produced by action of sodium rhodizonate with water solutions of the hydrochlorides of the bases. The precipitation reaction of ethylenediamine hydrochloride with sodium rhodizonate is very sensitive, and can be used in analysis. A spot reaction on paper will reveal as little as 0.3γ ethylenediamine through the formation of violet ethylenediamine rhodizonate.[9a] No more sensitive or surer test for ethylenediamine is known.

The Selective Activity of Pyrogallol and of Ortho-Situated Phenolic OH Groups

Causse[10] isolated and determined the compositions of compounds produced from trivalent antimony with pyrocatechol and pyrogallol, and one from bismuth with pyrogallol. Feigl and his collaborators[11] later showed that pyrogallol has considerable analytical importance. It can be used to precipitate antimony and bismuth quantitatively from mineral acid solutions; pure crystalline compounds that are white and yellow, respectively, are formed. Pyrogallol exhibits here a highly selective action since, under these conditions, it does not produce precipitates with other metal ions. This selectivity is the basis of gravimetric methods for determining antimony and bismuth. This reagent can also be applied in separating these metals from arsenic and lead, always a bothersome task if the classical methods are used.

The antimony compound of pyrocatechol is far more water-soluble than the pyrogallol compound. Its empirical composition corresponds to that of a pyrocatechol ester of antimonous acid (I).[12] The isomers of pyrocatechol (hydroquinone and resorcinol) are without action on solutions of antimonous salts because, in contrast to pyrocatechol, they lack the adjacent OH groups that are requisite for ring closure. Causse, and originally also Feigl, assumed the constitution of the antimony-pyrogallol compound to be analogous to that of the antimony-pyrocatechol compound, indicating, accordingly, that two adjoining OH

[9a] F. Feigl and H. E. Feigl, unpublished studies.

[10] H. Causse, Compt. rend. 114, 1072 (1892).

[11] F. Feigl, Mikrochemie 1, 74 (1923); Z. anal. Chem. 64, 41 (1924); F. Feigl and H. Ordelt, Z. anal. Chem. 65, 448 (1925).

[12] Bismuth salts do not form a precipitate with pyrocatechol. Instead, a yellow color results due to the production of the complex bismuth-pyrocatechinic acid, $H[Bi(C_6H_4O_2)_2]$.

groups of pyrogallol are essential for the precipitating action.[13] However, there are cogent reasons for not formulating this product as the antimonous ester of pyrogallol. It is more probably a hydrate (II), isomeric with the ester of antimonous pyrogallate and analogous to bismuth pyrogallate (III):
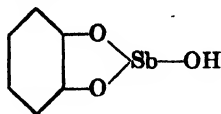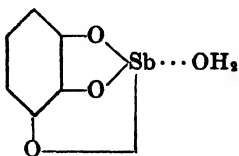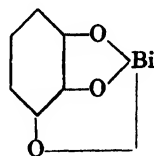
(I)   (II)   (III)

The analogous analytical behavior of Sb^{+++} and Bi^{+++} ions toward pyrogallol is not the only thing that is expressed by the analogous salt formulas of the antimony and bismuth pyrogallates. This formulation of antimony pyrogallate also explains the great differences in the water solubility of the Sb pyrogallol and the Sb pyrocatechol compounds. As stated, the Sb pyrocatechol compound is considerably more water-soluble than the pyrogallol compound. If their constitutions were alike, it would be logical to expect the pyrogallol compound to be not less soluble, but rather more so than the pyrocatechol compound, because in pyrogallol there is a residual free phenolic OH group which can be hydrated, and which therefore can promote solubility. In agreement with this concept, is the fact that 1,2,4-trihydroxybenzene, which is isomeric with pyrogallol, does not have the same precipitation capability toward antimony (and bismuth) salts as pyrogallol. It behaves toward antimonous salts as pyrocatechol does, though to a lesser degree. No action toward antimony (and bismuth) salts is exhibited by 1,3,5-trihydroxybenzene either, since it likewise lacks two adjacent OH groups. Christiansen[14] showed that the antimony precipitating action of the hydroxyl groups of pyrogallol is retained in gallic acid (3,4,5-trihydroxybenzoic acid) as well as in its esters and amides. The same behavior with respect to the ability to form slightly soluble bismuth compounds can be expected of gallic acid, although the actual trials have not yet been made. Since the aliphatic trihydroxy compound glycerol has no precipitating action on antimony and bismuth salts, the available evidence makes it likely that at least two OH groups, situated *ortho* to each other, are necessary if aromatic polyhydroxy compounds are to form

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[13] F. FEIGL, in his papers on the analytical use of pyrogallol, when explaining the specific precipitating action, simply assumed that inner complex salts were formed. Since reliable evidence was unavailable then, no attempt was made to formulate the products as inner complex salts.

[14] W. G. CHRISTIANSEN, *J. Am. Chem. Soc.* **48**, 1365 (1926).

slightly soluble antimonous salts.   Antimonous esters of the polyhydroxy compounds are produced in this case.   The formation of analogously constructed normal slightly soluble antimony and bismuth salts is possible when three *ortho*-situated OH groups.are available; the metal then replaces their H atoms.[14a]

Proceeding from the group action displayed toward antimony by pyrogallol and pyrocatechol, Wenger and his co-workers[14b] found that 9-methyl-2,3,7-trihydroxy-6-fluorone (IV) is a specific reagent for antimony.   This compound, which is soluble in alcohol, can be considered, with respect to its constitutional formula, as a derivative of pyrocatechol:
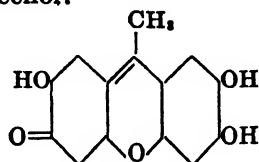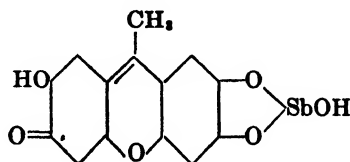
(IV)   (V)

It forms a red compound (V) with antimony salts in strongly acid solutions.   The reagent may also be used in spot tests; 0.2γ Sb can be detected in drops.

This discovery of the fluorone reagent shows that a knowledge of the activity of certain atomic groups aids greatly in the search for improvements in the analytical value of an organic reagent.   Similar examples of improvements due to supplementary chromotropic effects will be discussed later (see pp. 292, 330).   It will suffice here to note that colored water-soluble derivatives of pyrogallol (perhaps those with —N(CH$_3$)$_2$ groups) will probably behave toward antimony and bismuth like the parent substance.   The author has already found an analogous precipitating action in the case of halogen substituted pyrogallols.

Kieft and Chandlee[14c] studied the behavior of gallic acid (3,4,5-trihydroxybenzoic acid).   It is an excellent precipitant for bismuth, but antimony is only partially brought down by this reagent.

The Germanium–Specific Action of 9-Phenyl-2,3,7-Trihydroxy-6-Fluorone

The action of 9-methyl-2,3,7-trihydroxy-6-fluorone as a reagent for trivalent antimony was just discussed.   This "methylfluorone" pro-

[14a] S. Takagi and Y. Nagase [*J. Pharm. Soc. Japan* 56, 161, 170 (1936)] advanced an interesting complex chemical view of the structure of bismuth pyrogallate, which may be extended to the constitution of the antimonous salt.

[14b] P. Wenger, R. Duckert and Ch. R. Blancpain, *Helv. Chim. Acta* 20, 1427 (1937).

[14c] L. Kieft and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.* 8, 392 (1936). Compare also L. Rossi and A. T. Serantes, *Chem. Abstracts* 39, 475 (1945).

duces colored precipitates or colorations with numerous other metal ions. This action may be due, as can be seen from the structural formula, to the presence of the group $\diagdown$C(OH)—CO— in addition to the Sb-binding group. In fluorones, it is possible to have salification of the H atom with simultaneous coordination on the O-atom in the 5-position. Gillis and his associates[15] have now found that, in 1 N hydrochloric acid solution, the action of methylfluorone is limited to Sb, Sn, Ge, Mo, and V. They have established the conditions under which antimony can be detected with great selectivity by means of a spot reaction on filter paper impregnated with the reagent.

These workers[15a] have also studied the behavior of analogous fluorones, which contain C_6H_5, C_6H_4OH (o,m,p), $C_6H_3(OH)_2$ (m,p) in place of the methyl group. All these compounds, as well as methylfluorone itself, are colored. They are insoluble in water, and dissolve slightly in alcohol to produce yellow solutions. The following table contains the results of spot reactions, carried out on a spot plate, with 0.1% alcoholic solutions of the various fluorones and 1% salt solutions, which were 1 N with respect to free hydrochloric acid. (* Indicates that a precipitate was formed.)

Metal	Methyl	Phenyl	o-Hydroxy
Sb^{III}	Bright-red*	Carmine*	Orange-red*
$Sn^{II, IV}$	Yellow	Orange*	Orange
Ge	Orange*	Orange-red*	Orange.*
Mo	Brown-red*	Bright red*	Dark red*
V	Gray*	Black-brown*	Brown*
Fe^{III}	Yellow	Orange	Yellow
Ti	Yellow	Pink*	Yellow
Zr	Orange	Orange-red*	Yellow

Metal	m-Hydroxy	p-Hydroxy	Dihydroxy (m,p)
Sb^{III}	Carmine*	Bright red*	Bright red*
$Sn^{II, IV}$	Orange	Orange	Yellow
Ge	Orange*	Orange*	Orange-brown
Mo	Bright red*	Bright red*	Red-brown*
V	Gray-brown*	Black*	Brown*
Fe^{III}	Yellow	Yellow	Yellow
Ti	Yellow	Orange	Yellow
Zr	Orange	Yellow	Yellow

[15] J. GILLIS, J. HOSTE and A. CLAEYS, *Anal. Chim. Acta* 1, 291 (1947).
[15a] J. GILLIS, J. HOSTE and A. CLAEYS, *Med. Vlaamsche Acad.* 9, 1 (1947).

Accordingly, in acid solution, acid-forming metals react especially with fluorones. Nothing is known as yet about the composition of the reaction products with Sn, Ge, Ti, Zr, Mo, and V. Possibly they involve double compounds of fluorones with metal salts or metal acids, the latter of the type of heteropolyacids. The possibility is not excluded of the production of inner complex phenol esters with metal acids through the action of the $=C(OH)-CO-$ groups contained in the fluorones. (It may be expected that the tendency of this group to form inner complexes will also be exhibited in ammoniacal and alkaline solutions of fluorones.) Finally, the possible formation of adsorption compounds (compare Chapter X) between hydrolysis products of the respective metal salts and fluorones must be taken into account.

Special significance attaches to a further observation by Gillis and his coworkers. They found that the reaction products of germanium with methyl-, phenyl-, and hydroxyfluorones are very acid-stable. Whereas the products obtained by the action of all the other metals with fluorones are immediately decomposed by 6 N hydrochloric or nitric acids, the germanium compounds, once formed, resist even 11 N acid. This difference was made the basis of tests for germanium that are strictly specific. These workers recommend phenylfluorone (9-phenyl-2,3,7-trihydroxy-6-fluorone) which produces a red acid-stable germanium compound. They describe[15c] a spot reaction on paper impregnated with this reagent which reveals germanium at a dilution as high as 1:500,000.

Analytical Behavior of 8-Hydroxyquinoline (Oxine) and Its Derivatives

Hahn[16] was the first to report that 8-hydroxyquinoline can be used for the gravimetric determination of aluminum, zinc, and magnesium. He also proposed the name "oxine" for this reagent.[17] Soon thereafter Berg[18] began to publish his numerous fundamental studies of the varied analytical uses of oxine and thus opened its extensive field of application. Despite the non-specificity of its salt-forming abilities, oxine now shares with dithizone (see p. 241), which likewise is not specific, the honor of being the most widely used organic reagent for inorganic determinations. This situation has become possible only because both of these reagents exhibit extensive selective actions provided their use is combined with a careful adjustment of the pH values and a judicious use of masking agents. They then often offer fairly simple solutions for many difficult analytical problems.

[15c] J. Gillis, J. Hoste and A. Claeys, *Anal. Chim. Acta* **1**, 302 (1947).

[16] F. L. Hahn, *Z. angew. Chem.* **39**, 1198 (1926).

[17] F. L. Hahn and K. Vieweg, *Z. anal. Chem.* **71**, 122 (1927).

[18] R. Berg, *J. prakt. Chem.* **115**, 178 (1927).

Oxine (I) is a colorless crystalline compound that is only slightly soluble in water. Its colorless solutions in anhydrous organic solvents turn yellowish with even small amounts of water. This color may arise from a change in constitution producing the quinoidal form (II).[19] An equilibrium is probably established between the tautomeric forms:

(I)   (II)
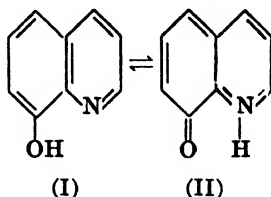
Acetic acid, alcohol, and acetone are the most common solvents for this reagent. Oxine, as shown by (I), has an amphoteric character; it is acidic by virtue of its phenolic component, and basic because of its pyridine component. Its salts with mineral acids are water-soluble. The mole weight of the base is high and accordingly it forms insoluble salts with complex metallo-acids and certain heteropolyacids. Quantitative determinations of phosphorus and bismuth are based on the oxine salts of phosphomolybdic acid[20] and hydroiodobismuthic acid.[21] The salt-forming ability arising from the phenolic nature of oxine, and the proximity of the phenolic OH group to the cyclic bound nitrogen atom, are more important from the analytical standpoint. In acetic acid solutions, buffered with acetate, oxine forms insoluble, more or less colored salts with many metals (see Table II). Most of these precipitates are quite soluble in organic liquids, especially chloroform, and thus they reveal their membership in the class of inner complex salts. Structure (III) is assumed for them; this corresponds to the phenol formula (I). However, arguments can also be advanced in favor of (IV), which corresponds to the formulation of oxine as a quinone (II):

(III)   (IV)

(Me = 1 equivalent of metal)
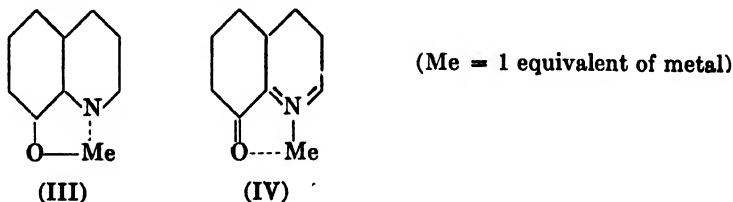
Formulation (IV) is not only supported by the change in color when water is introduced into solutions of oxine in organic liquids (*vide supra*),

[19] P. PFEIFFER, Organische Molekülverbindungen, p. 418, Stuttgart, 1927.
[20] R. BERG, Z. angew. Chem. 41, 611 (1928); Chem. Ztg. 52, 449 (1928).
[21] R. BERG and O. WURM, Ber. 60, 1664 (1927).

TABLE II

Action of Oxine

Metal	Color of oxinate	pH range for complete precipitation[a]	Solubility in chloroform[b]	Concentration limit of tests[*]		
				Acetic acid-acetate solution	Ammonia-tartrated solution	Sodium hydroxide-tartrated solution
Aluminum..... .	Greenish-yellow	4.2–9.8	S	1:310,000	1:178,000	
Bismuth..... ..	Orange-yellow	4.8–10.5	S	1:307,000	1:217,000	
Cadmium.... .	Yellow	5.4–14.6	S	1:416,000	1:200,000	1:104,000
Calcium...	Light yellow	9.2–13	I	....	1:120,000	
Cobalt..... .	Flesh colored	4.3–14.5	S	1:312,000	1:100,000	
Copper.	Light yellowish-green	5.3–14.6	S	1:630,000	1:410,000	1:270,000
Gallium..	Light yellow	ca. 6–8	S	....	1:400,000	
Indium....	Light yellow	Acetic acid acetate	S ?	1:500,000		
Iron (III)...	Green-black	2.8–ca. 12	S	1:384,000	1:238,000	
Lead.............	Greenish-yellow	8.4–12.3	S	1:80,000		
Magnesium........	Greenish-yellow	9.4–12.7	I	....	1:410,000	1:270,000
Manganese......	Dull yellow	5.9–10.0	S	1:357,000	1:172,000	
Molybdenum[c]. .	Yellow-orange	3.6–7 3	I	1:100,000		
Nickel..... ...	Yellow-green	4.3–14.6	S	1:256,000	1:200,000	
Palladium...	Orange-yellow	Dilute HCl	S	1:402,000		
Thallium (III)[d] ...	Lemon-yellow	6–8	S	1:200,000		
Thorium........ .	Lemon-yellow	4.4–8.8	S	1:170,000		
Titanium[e].... ...	Orange-yellow	4.8–8.6	S	1:300,000	,1:80,000	
Tungsten[f]..... .	Yellow	5.0–5.7	I	1:500,000		
Uranium[g].... ..	Red-brown	5.7–9.8	S	1:239,000	1:200,000	
Vanadium[h]. . ..	Green-brown-black	Acetic acid acetate	S	1:600,000		
Zinc......... . .	Greenish-yellow	4.6–13.4	S	1:1,000,000	1:277,000	1:140,000
Zirconium........	Light yellow	Acetic acid acetate	S	1:600,000		

* The values might well be rounded off; e.g., 1:300,000 instead of 1:310,000.

[a] Values for Co, Cu, Mg, Ni, W, U and Zn from H. R. FLECK and A. M. WARD, Analyst **58**, 3888 (1933); most of the others from H. GOTO, J. Chem. Soc. Japan **54**, 725 (1933); **56**, 314 (1935).

[b] S = extracted, I = not extracted. Compare footnote 22a.

[c] Formula of hydroxyquinolate = $MoO_2(C_9H_6ON)_2$.

[d] Data regarding thallium oxinate from F. FEIGL and L. BAUMFELD, Anal. Chim. Acta **2**, 430 (1948).

[e] $TiO_2(C_9H_6OH)_2$.

[f] $WO_2(C_9H_6ON)_2$.

[g] $UO_2(C_9H_6ON)_2 \cdot C_9H_7ON$.

[h] $V_2O_5(C_9H_6ON)_4$.

but also especially by the excellent solubility of many metal oxinates in chloroform and other organic solvents. The solubility rule (p. 409) states that inner complex metal salts are quite soluble in chloroform only when the salt molecule contains *no* free acidic or basic groups. A comparison of (III) and (IV) reveals that this is the case only in the quinoid formulation, since the basic nitrogen atom of the quinoline component is still present in (III).[22] An explanation of the departure from the

[22] The inner complex salts of quinaldinic acid show clearly that the basic nitrogen atom of quinoline in inner complex salts is related to their insolubility. The coordina-

solubility rule in the case of the solid metal oxinates, however, does not necessarily require the postulation of a tautomerism between (III) and (IV). It is more likely that form (III) is produced initially and dissolves to a slight extent in chloroform. Only then, *i.e.*, in this solution, does the rearrangement into (IV) take place. Thus the equilibrium:

$$\text{Me oxinate (III)} \rightleftharpoons \text{Me oxinate (III)}$$
(solid)   (dissolved)
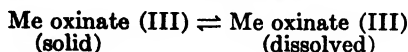
is constantly disturbed by the subsequent rearrangement:

$$\text{Me oxinate (III)} \rightarrow \text{Me oxinate (IV).}$$
(dissolved)   (dissolved)
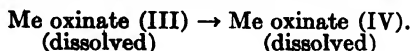
The result is a simulated solubility, which actually is not a characteristic of the form (III) *per se*. The fact that chloroform-insoluble oxinates are known (see Table II) can be brought into harmony with this hypothesis if it is either assumed that these oxinates are represented exclusively by (III), or that they are normal rather than complex salts.[22a]

tion formula of the inner complex quinaldinates   demonstrates that
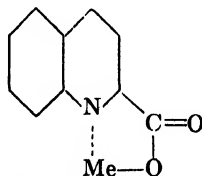
these are practically identical with the oxinates with respect to the inner complex ring when the latter are represented by (III). However, in contrast to the metal oxinates, the metal quinaldinates are insoluble in chloroform.

[22a] Studies by F. FEIGL, H. W. ZOCHER and C. TÖRÖK [*Anal. Chim. Acta* 2, in press] showed that the solubility in chloroform of metal oxinates depends on their content of bound water and the tenacity with which it is held. Oxinates which come down in the anhydrous form (Fe, Al, Cu, In, *etc.*) can be extracted by chloroform. This is also true of the oxinates of Bi, Co, and Ni, which carry 1–2 molecules of water of crystallization capable of release even at moderate temperatures. In contrast, the oxinates of Zn, Cd, and Mg are not extractable with chloroform; the water is held more firmly in these cases. However, it is given up on heating to 130–140°C., and the anhydrous materials then dissolve in chloroform. The loss of water is accompanied by a color change from pale yellow (green fluorescence) to yellow (yellow fluorescence). It should also be pointed out here that some inner complex metal oxinates contain water of crystallization. It is often assumed that the binding power of the metal atom is exhausted in inner complex salts and consequently no further coordination can occur on it (compare F. J. WELCHER, *op. cit.*, vol. I, p. 23). This idea is obviously not correct. The binding of two molecules of water in the hydrates of the oxinates of divalent metals (Mg, Cd, Mn, Co, Ni) can be explained by an increase in the coordination number of the metal from 4 to 6. On the other hand, it is difficult to state the coordination positions in the hydrates of oxinates of trivalent metals. $Bi(C_9H_6NO)_3 \cdot H_2O$ is known, and F. FEIGL and L. BAUMFELD [*Anal. Chim. Acta* 2, in press] have isolated $Tl(C_9H_6NO)_3 \cdot 3H_2O$. The water is held so firmly in the thallium oxinate that, on heating above 110°C., there is partial hydrolysis to

The formulation of inner complex salts according to (III) and (IV) holds throughout for di- and trivalent metals.   Their oxinates frequently carry water of crystallization, which is given up at higher temperatures. Among the quadrivalent metals only the thorium compound corresponds to this composition, *i.e.* to the replacement of four acidic hydrogen atoms. The oxine compounds of titanium^{IV}, Mo^{VI}, and W^{VI} correspond in their composition to the phenolic esters of the respective metalloacids (compare Table II).   Probably the same is true of niobic and tantalic acids.   The mercury compound, investigated by Berg,[23] falls entirely outside any of the known salt types of oxine.   According to its empirical formula HgC$_9$H$_6$NO·2H$_2$O, it contains one atom of mercury for each molecule of oxine.[24]

Table II contains typical characteristic data concerning metal oxine precipitations.

Oxine, as indicated by the table, is almost a universal precipitant for metals in acetic acid-acetate solution.   Selectivity appears only on adjusting the pH, on applying masking agents, or both.   In this connection, it is interesting to note the great differences, as shown in the table, in the precipitation picture in the presence of the same masking agent (tartrate) when the solution is made alkaline with ammonia and sodium hydroxide, respectively.   By combining certain pH values and masking agents it has been found possible to accomplish in simple fashion many separations of metal ions, which otherwise present great difficulty.   For instance, it is possible to detect and determine aluminum and iron in solutions containing phosphate, tartrate, oxalate, or malonate, where the normal precipitation of the hydrated oxide is not possible.   The analytical use of oxine is not confined to gravimetric procedures in which metal oxinates are weighed.   The oxine combined in the precipitates, or the unused portion of a measured excess of the reagent, can be determined titrimetrically (with bromine) or colorimetrically.   Both procedures are based on the phenolic nature of oxine.   A new type of titration, which is not based on the phenolic nature, but on an oxidative splitting of the oxine in the benzene ring appears to be possible.   Ceric or permanganate

Tl(OH)$_3$ along with loss of water.   Further evidence against the assumption of coordinative saturation in inner complex salts is found in the stable oxine compounds UO$_2$(C$_9$H$_6$NO)$_2$·C$_9$H$_7$NO and Th(C$_9$H$_6$NO)$_4$·C$_9$H$_7$NO.   In these, oxine molecules are assumed to be coordinated on inner complex salts.

[23] R. Berg, *J. prakt. Chem.* **115**, 181 (1927).

[24] Probably this is not a compound of univalent mercury.   It is more likely that a partial mercuration of the nucleus has occurred.   An insoluble silver salt, [HgC$_9$H$_6$NO(OH)$_3$]Ag$_2$ precipitates from mineral acid solutions, which could be the silver salt of an hydroxo acid.

solutions are used as oxidants in sulfuric acid solution. 1,2-Pyridine carboxylic acid is formed.[25] Colorimetric determinations make use of (a) the ability of the phenolic oxine to react with the complex phosphotungstic or phosphomolybdic acid to produce soluble, intensely blue lower oxides of tungsten and molybdenum, or (b) the ability of the phenolic oxine to couple with diazo compounds to produce alkali-resistant dyes that can be compared colorimetrically. Sandell[26] showed that the fluorescence of gallium, aluminum, indium, and zinc oxinates in chloroform solution can also be utilized for quantitative purposes. A consideration of the many and varied possible applications of this reagent lies beyond the scope or this book. The extensive literature should be consulted for more detailed information.[27]

A study of the behavior of derivatives of oxine will aid in securing a better understanding of the activity of certain atomic groupings in organic reagents. Even though the salt-forming group is retained in both series, these oxine derivatives form two distinct sets of compounds, because a substitution is possible in either the phenol or pyridine component. Up to the present, the phenol-substituted derivatives have received most of the attention simply because they are more readily available. It has been learned by experience that the introduction of inorganic substituents enhances the selective action more than the introduction of organic groups. Berg[28] studied numerous oxine derivatives with respect to their precipitating action. He found for example, that the two halogenated oxines: 5,7-dichloro-8-hydroxyquinoline (chloroxine), and 5,7-dibromo-8-hydroxyquinoline (bromoxine), form insoluble inner complex salts with iron (black-green), titanium (orange-yellow), copper (green-yellow), and vanadium (brown). These products do not exhibit any marked difference in color when compared with the corresponding normal oxinates. They do, however, show great differences with respect to resistance toward acids. The normal oxinates are not stable against higher concentrations of acetic acid, whereas the salts of chloroxine and bromoxine are not attacked by even dilute mineral acids. The latter salts form crystalline precipitates at dilutions as great as 1:1,000,000, and, because of their low percentage content of metal, can be used

[25] Compare T. F. DROZD, *Chem. Abstracts* **30**, 7486 (1936); G. F. SMITH and H. H. WILLARD, *ibid.* **35**, 2438 (1941).

[26] E. B. SANDELL, *Ind. Eng. Chem., Anal. Ed.* **13**, 844 (1941).

[27] R. BERG, Die analytische Verwendung des *o*-Oxychinolins (Oxin) und seiner Derivate, 2nd ed., Stuttgart, 1938. W. PRODINGER, Organic Reagents Used in Quantitative Inorganic Analysis (Translated by S. Holmes), p. 103 *ff.*, Elsevier Publishing Co., New York, 1940. See also G. E. LUNDELL and H. B. KNOWLES, *Bur. Standards J. Research* **3**, 86 (1929) and F. J .WELCHER, *op. cit.*, Vol. I.

[28] R. BERG, *Z. anorg. allgem. Chem.* **204**, 208, 215 (1932).

successfully in accurate micro gravimetric determinations.[29]   Bromoxine permits a further increase in selectivity, because, when tartaric, citric, or malonic acid is present, the precipitation of titanium is prevented, while copper and iron come down as usual.   This fact has been employed particularly to separate iron and titanium.   Oxalic acid prevents the precipitation of iron as well as of titanium, but not of copper, so that in oxalic acid solution bromoxine is a special reagent for copper.

A very interesting derivative of oxine with inorganic substitutents in the phenol component is 7-iodo-8-hydroxyquinoline-5-sulfonic acid (I). This light yellow acidic compound is fairly soluble in water, forming orange-yellow solutions.   It shows no reaction with ferrous solutions, but at pH *ca.* 2.5 it produces an intense blue color with ferric salts.   Since the color exhibits its maximum intensity at the ratio 1 Fe: 3 oxine, Yoe,[30] the discoverer of this reagent, correctly concluded that a water-soluble inner complex compound (II) is formed:

(I)   (II)
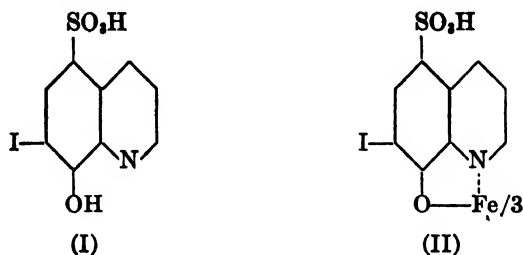
This reagent reacts with numerous metal ions to form soluble or, in some cases, even slightly soluble salts (see p. 188).   However, with the exception of vanadium,[31] with which it produces a brown coloration, ferric iron is the only material that gives á color reaction with this substituted oxine. ´ As a color reagent, it is thus practically specific for iron and hence Yoe has named it "ferron."   It is an excellent example of the fact that a reagent can possess a specific or selective analytical effect, without the underlying salt formation *per se* being specific or selective.   The detection of iron succeeds at a dilution as great as 1:10,000,000, and hence ferron is one of the most sensitive reagents for iron.   This extreme sensitivity is emphasized by the fact that ferron gives a positive iron reaction with acid solutions that contain phosphate, even though the iron is then so firmly bound in the $[Fe(PO_4)_2]^{---}$ anions that the familiar thiocyanate reaction does not occur.   In pure ferric solutions, the iron can be accu-

[29] R. Berg, and H. Küstenmacher, *Mikrochemie, Emich Festschrift* 1930, p. 26; see also L. W. Haase, *Z. anal. Chem.* 78, 113 (1930).

[30] J. H. Yoe, *J. Am. Chem. Soc.* 54, 4139 (1932); J. H. Yoe and R. T. Hall, *ibid.* 59, 872 (1937).

[31] J. Molland, *Chem. Abstracts* 34, 1932 (1940); *Compt. rend.* 210, 144 (1940).

rately determined colorimetrically by means of ferric ferronate. However, aluminum, tin, and other hydrolyzable metal salts interfere with this colorimetric measurement of iron, even though they do not affect its qualitative detection. Doubtless, the reason is that the reagent forms soluble complex salts with other metal ions.

Yoe (*loc. cit.*) found that copper salts form a white precipitate with ferron. Berg (*loc. cit.*) observed that precipitates are likewise produced with concentrated solutions of mercury and cadmium salts. Studies in the author's laboratory[32] have given the expected finding that the salt-forming ability of the parent compound, 8-hydroxyquinoline, is retained in ferron, and that it likewise can manifest this property against ions other than Fe^{+++}. However, in ferron, the SO_3H group is an additional factor and leads to interesting effects. The behavior of 0.5% metal salt solutions with ferron, and with this reagent in the presence of ammonia or soda, can be summarized thus:

(1) Cu, Pb, Sn^{II}, Sn^{IV}, Th, Zr, Bi, Hg^{I}, are precipitated at room temperature by ferron from neutral or weak mineral acid solutions. The precipitates are white or light yellow, and in some cases the precipitation is quantitative. If excess ferron is used, the precipitates, with the single exception of the lead compound, dissolve completely on warming. All of the precipitates are soluble in excess ammoniacal ferron solution. The copper and lead precipitates dissolve in sodium carbonate solution.

(2) Bi, Hg, Zr, Ce, Sn^{II}, Sn^{IV}, Ti, Th, Al, Fe, UO_2, in neutral or slightly acid solutions, when treated with excess ferron and then made ammoniacal, give clear solutions, which remain clear even after boiling. The same picture of a precipitation masking is obtained if an ammoniacal solution of ferron is added directly to solutions of the foregoing metals. Basic compounds of noncomplex character are also possibly present in ammoniacal metal-ferron solutions (Chapter IV, p. 97).

(3) Bi, Hg, Th, Ti, Zr, Al, Fe, Zn, Ag, in neutral or weakly acid solutions, on treatment with excess ferron and then alkalized with sodium carbonate, give solutions that remain clear even when boiled. The direct addition of a sodium carbonate solution of ferron to these salt solutions results in the same masking of the precipitation reactions.

The preceding qualitative experiments, both by the precipitation and solution reactions given in (1), and by the maskings against precipitation by ammonia or soda given in (2) and (3), indicate the formation of ferron salts. The precipitation reactions argue for the entrance of the metal as cation in a ferron salt; the solution and masking reactions favor the inclusion of the metal in stable complex anions. Analyses of the copper and lead precipitates show that the metal:ferron ratio is 1:1; while in

[32] F. Feigl, C. Machline and K. Sobia, unpublished studies.

the thorium precipitate the relation is 1 Th:2 ferron.   This ratio, in the case of divalent metals, corresponds to constitution (I) or (II)
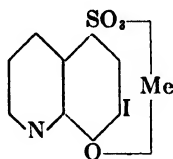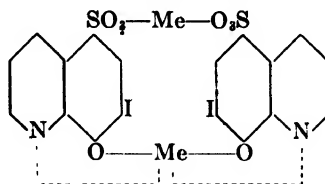
(I)   (II)

The writer believes (II) is the more likely formulation.   The solution of compounds containing cationically bound metal in solutions of ferron (with addition of ammonia, when necessary) is most likely due to the reaction:
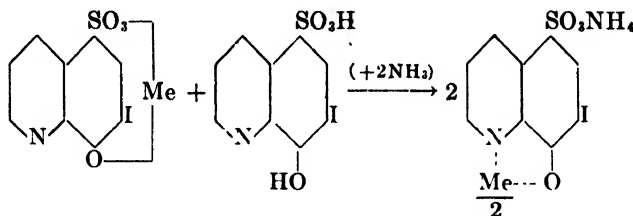
(or II)   (III)

Probably compounds of the foregoing type III, corresponding to the structure assigned to ferric ferronate by Yoe, are also formed in the experiments included in (2) and (3).   Accordingly, these cases involve the formation with ferron of soluble compounds, which contain inner complex anions.   These compounds, however, have structures entirely different from those with inner complex anions described in Chapter III. In the latter, the formation of inner complex anions involved acidic groups in such fashion that metal atoms were linked to these groups by both principal and auxiliary valences.   In the ferron inner complex anions, the acid SO_3H group has remained completely independent and acts as such, or in the form of its ammonium or alkali salt, as the solubility-promoting vehicle.   In conformity with the solubility rule (see p. 409), neither the ferric ferron compound nor the analogously constructed inner complex compounds are soluble in chloroform or other organic liquids.   Consequently, they cannot be extracted from their water solutions.   In this connection, it should be pointed out that the tendency of ferron to form inner complex anions is sometimes so marked that, for example, $Bi(OH)_3$ and $Pb(OH)_2$ easily dissolve in ammoniacal ferron solutions.   The resulting lead solution yields no precipitate of $PbSO_4$ on the addition of Na_2SO_4.   The silver-ferron compound in alka-

line (sodium carbonate) solution is stable against halide ions in the cold, and against chromate ions even though boiled. The copper precipitate [compare (1)] is easily soluble in sodium hydroxide if ferron is present. Consequently, the findings summarized in (1), (2), and (3) indicate definitely that ferron, in solutions of various pH values, will lend itself to a number of applications as a new masking agent.[33]

Studies of the behavior of homologues of ferron, with substituents other than iodine in the 7-position, as well as of the sulfonic acid itself, have been made by Molland.[34] He was particularly interested in the possible use of these reagents in the colorimetric determination of iron. He observed that ferric iron gives a blue color with 8-hydroxyquinoline-5-sulfonic acid, 7-bromo-8-hydroxyquinoline-5-sulfonic acid, and 7-chloro-8-hydroxyquinoline-5-sulfonic acid. A brown color results when ferric solutions are treated with 7-nitro-8-hydroxyquinoline-5-sulfonic acid, or 7-nitroso-8-hydroxyquinoline-5-sulfonic acid. Molland found that certain metal ions interfere, and likewise complex-formers for iron. He noted also that the nitroso derivative of the sulfonic acid gives a precipitate with lead and also with alkaloids. He believes these observations have analytical promise.

Gutzeit and Monier[35] were the first to use derivatives of 8-hydroxyquinoline with organic substituents in the phenol component. They worked with the azo compounds of oxine. These are readily obtained because the phenolic oxine readily couples in the 5-position with diazotized aromatic amines. The products are (acid) dyes:
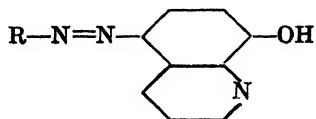
and their color quality is transmitted to their respective metal salts. Since R can be widely varied, a great number of these substituted oxines is possible. When tested, they showed useful selective action toward mercuric and palladium ions, especially if the amine used in the diazotization and coupling also contained sulfo groups. These azo dyes were used by Gutzeit and Monier as spot test reagents, but their merits were slight. The intense color of the reagents, and the inconsiderable color differences,

[33] It should be pointed out that among the ferron complex salts present in ammoniacal solution, only the Ni, Cd, and Zn compounds are masked against precipitation with oxine. Solutions of the other ferron complex salts yield quantitative precipitates of the various metal oxinates.

[34] J. MOLLAND, Chem. Abstracts **36**, 6939 (1942); compare also J. Am. Chem. Soc. **62**, 541 (1940).

[35] G. GUTZEIT and R. MONIER, Helv. Chim. Acta **16**, 233, 478, 485 (1933).

if any, between the metal salt and the reagent, militate against an effective discernment of small quantities of precipitates.

More interest attaches to the procedure in which the oxine, derived from a previously isolated oxinate, is readily converted into an azo dye. This is the basis of the method used by Alten and his collaborators[36] for the colorimetric determination of aluminum and magnesium. The method doubtless can be applied to other oxinates. The precipitate is washed, dissolved in hydrochloric acid, diazotized with alkali nitrite, and coupled with sulfanilic acid. The resulting azo dye is soluble in sodium hydroxide. The solution can then be compared colorimetrically with standard dye solutions prepared by an analogous procedure.

Among the oxine derivatives containing a substituent in the phenol component having dyestuff characteristics is the so-called indoxine (I). It is easily prepared and has been studied by Berg and Becker.[37] This quinone-imine dye has indicator properties; green in alkali, red in acid solutions. The transition range covers pH 6 to 8. An ammonium salt (II) probably is present in acid solutions:

(I)   (II)
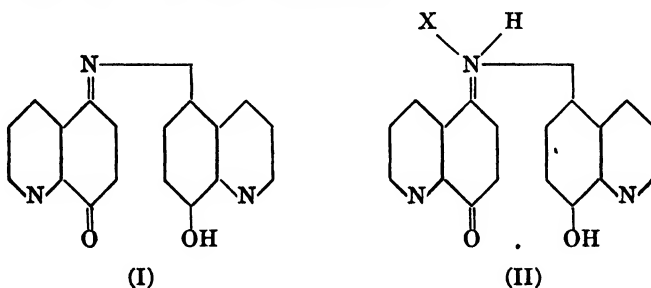
The metal salts of indoxine, which precipitate from acid solutions, are blue to violet. Consequently, in contrast to the azo derivatives of oxine, there is a distinct-color difference between the reagent solution and the reaction product, a fact that considerably raises the analytical value of this reagent. Berg and Becker (*loc. cit.*) showed that interesting analytical applications are feasible with indoxine despite its slight solubility in water. For instance, it serves as indicator, in acetic acid solutions, for the argentimetric titration of chloride, bromide, iodide, or thiocyanate. The first drop, in excess, of silver nitrate produces a blue-green coloration, because of the formation of silver indoxinate. Titrimetric determinations of cobalt, nickel, and other metals can be carried out in acetic acid solutions, since an excess of the reagent renders the filtrate from the precipitate pink. These workers also found it possible to carry out selective

[36] F. ALTEN, H. WEILAND and B. KUREMIES, *Z. angew. Chem.* **46**, 668, 697 (1933).
[37] R. BERG and E. BECKER, *Ber.* **73**, 172 (1940); *Z. anal. Chem.* **119**, 81 (1940).

titrations involving precipitation by indoxine in the presence of suitable masking agents.

The following findings are available regarding oxine derivatives with substituents in the pyridine component. Berg[38] found that 2-phenyl-8-hydroxyquinoline-4-carboxylic acid forms a yellow mercury salt (1:200,000) in dilute nitric acid. Since it is the only metal giving this result, the test is specific under these conditions. Merritt and Walker[39] studied 2-methyl-8-hydroxyquinoline (8-hydroxyquinaldine) as a precipitant. They found that the ability to form a salt with aluminum had been lost in this derivative. They ascribe this heightened selectivity to a size effect, due to the methyl group (see p. 425). Hence there is no doubt that substitution, in either the phenol or pyridine component of oxine, affects the salt-forming ability of the active group and also the properties of the metal salts. It is quite possible, therefore, that oxine derivatives with substituents in both components will exhibit interesting analytical effects. However, such studies will be considerably hampered by the difficulty of preparing suitable compounds.

The Selective Action of 4-Hydroxybenzothiazole

The examples already given, and the numerous ones to follow, show that the selective effects of organic reagents are invariably related to the presence of certain salt-forming groups and coordinatable atoms. However, it may be seen from the statements in the preceding section concerning the behavior of derivatives of 8-hydroxyquinoline, that selectivity is not exclusively a matter of the presence of certain groups, but that other groups of the molecule can exert an influence. Erlenmeyer and his associates[39a] have made a valuable contribution to our knowledge of the dependence of a group action on the remainder of the molecule of an organic compound. They studied the synthesis of 4-hydroxybenzothiazole and tested its analytical behavior. A comparison of the structural formulas of 4-hydroxybenzothiazole (I) and 8-hydroxyquinoline (II) shows that both contain the same phenol component in the same adjacent position to a coordinatable, cyclically bound nitrogen atom. They differ, in a purely structural sense, with respect to an alteration of the pyridine component. In (I) there has been substitution of a —CH=CH— group of the pyridine ring by an aromatic sulfur atom. As a result, the position of the carbon double bond is firmly fixed in

[38] R. BERG, Z. anorg. allgem. Chem. 204, 208 (1932).
[39] L. L. MERRITT and J. K. WALKER, Ind. Eng. Chem., Anal. Ed. 16, 387 (1944).
[39a] H. ERLENMEYER and H. UEBERWASSER, Helv. Chim. Acta 21, 1695 (1938); H. ERLENMEYER, H. UEBERWASSER and H. WEBBER, ibid. 21, 709 (1938); H. ERLENMEYER and E. H. SCHMIDT, ibid. 24, 1159 (1941).

4-hydroxybenzothiazole, whereas in 8-hydroxyquinoline (oxine) the double bonds can oscillate as shown in (IIa) and (IIb).

Me $= \frac{1}{2}$ Cu, Ni, Zn, etc

(I)   (IIa)   (IIb)   (III)
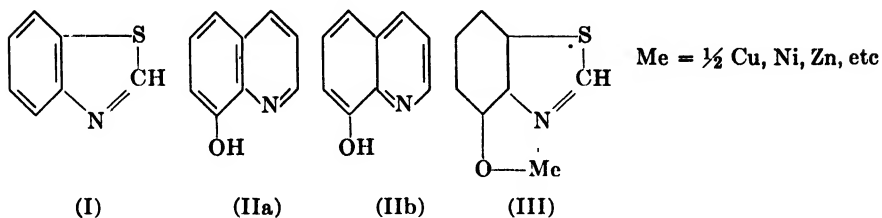
These two amphoteric compounds could be expected to exhibit similar analytical behavior, as they both contain the same salt-forming groups (phenolic OH adjacent to a basic nitrogen atom). However, this is only partly true. It is true that 4-hydroxybenzothiazole, like oxine, forms inner complex salts with numerous metal ions in acetic acid-acetate buffered or alkaline solutions. However, these salts are not as water-insoluble in all instances as is the case with the analogous oxinates. Thus, the solubility of aluminum 4-hydroxybenzothiazolate is 30.5 mg./l. as opposed to 1.2 mg./l. for aluminum oxinate. Likewise, the magnesium salt of (I) is decidedly more soluble in water than the water-insoluble magnesium oxinate. The copper, zinc, and nickel salts of 4-hydroxybenzothiazole possess a low solubility that can be used analytically. In these cases, the analogy to the oxinates is so marked that the metals can be determined in absolutely the same manner as when oxine is used as the precipitant. In other words, the inner complex salts can be weighed as such, or the titrimetric procedure can be employed in which the organic component of the 4-hydroxybenzothiazolate is brominated. The bromination, as in the case of oxine, occurs in the 2,5 positions relative to the phenol group:

It is rather remarkable that titanium, vanadium, molybdenum, and tungsten, which give very sensitive precipitation reactions with oxine do not do so with 4-hydroxybenzothiazole, even in concentrated solution. Obviously, this is not due to differences in the solubility of the products but to true lack of reaction. Accordingly, 4-hydroxybenzothiazole, despite its possession of the same reactive groups, exhibits a far greater selectivity with respect to compound formation and precipitating action than oxine. The reasons for the differences in the analytical behavior of these two reagents are clearly to be sought in the differences in their physicochemical properties. The following data are pertinent:[9b]

[9b] The data for 4-hydroxybenzothiazole are taken from the publications of H. ERLENMEYER (loc. cit.) and from private communications of H. ERLENMEYER and M. BLUMER. The figures regarding oxine come from R. BERG, Das Oxychinolin, 2nd ed., Stuttgart, 1938.

	4-hydroxybenzothiazole	8-hydroxyquinoline
Solubility in 100 ml. water..........	800 mg.	520 mg.
Solution color in water..............	Colorless	Light yellow
pH in 2.6 × 10 M solution..........	4.24	6.77
Dissociation constant K_a............	8.0 × 10^{-10}	2.0 × 10^{-10}
Dissociation constant K_b.......... .	5.0 × 10^{-12}	1.0 × 10^{-10}
Isoelectric point....................	5.9	7.2

In the light of these figures, there is no doubt that in 4-hydroxybenzothiazole the acidic charácter due to the phenol component is more marked than in oxine. The acidifying effect stems from the cyclically bound sulfur atom. The tendency to form a quinoidal structure, to which the yellow color can be ascribed (see p. 182), is certainly less in 4-hydroxybenzothiazole than in oxine. It is probable that this tendency plays a part also in the formation of inner complex salts and is likewise a factor in their true structure. This is indicated by the very noteworthy fact that the copper, nickel, and zinc salts of 4-hydroxybenzothiazole, in contrast to the corresponding oxinates, are not soluble in chloroform.[39c] In this connection, see the remarks on p. 184 regarding the solubility of oxinates in chloroform.

The more pronounced acid character of 4-hydroxybenzothiazole makes its non-reactivity toward acid-forming metals plausible. It was stated that the oxinates of titanium, vanadium, molybdenum, and tungsten have constitutions differing from those of the true oxinates. They are phenolic esters of the respective metal acids and are not metal salts. However, these esters are not formed directly but insoluble oxinates of the particular metal acids are the initial products. This has been proved in the case of vanadium[39d] by the isolation of the yellow compound $(C_9H_7NO)_2·H_2V_4O_{11}$, and correspondingly for tungsten by means of the red compound $(C_9H_7NO)·H_2WO_4·3H_2O$.[39e] The vanadium compound is the oxine salt of tetravanadic acid, the tungsten compound is an acid (mono) oxine salt of tungstic acid. These oxine salts go over into the blue-black $V_2O_3(C_9H_6NO)_4$ and the yellow $WO_2(C_9H_6NO)_2$, which are viewed as oxine esters (phenol esters) of divanadic and tungstic acids, respectively. The transformation of the insoluble oxine salt into the insoluble oxine ester occurs by intramolecular loss of water. The

[39c] Private communications from H. ERLENMEYER and M. BLUMER.

[39d] R. MONTEQUI and M. GALLEGO, Chem. Abstracts **28**, 3409 (1934); see also S. ISHIMARU, ibid. **28**, 3681 (1934).

[39e] W. D. TREADWELL and R. NIERICKER, Helv. Chim. Acta **29**, 1474 (1946); compare also E. OTERO and R. MONTEQUI, Chem. Abstracts **29**, 3937 (1935); H. GOTO, ibid. **32**, 7368 (1938).

production of salt and the subsequent formation of ester can be represented by the following scheme.   Molybdic acid[39] is used as a model,
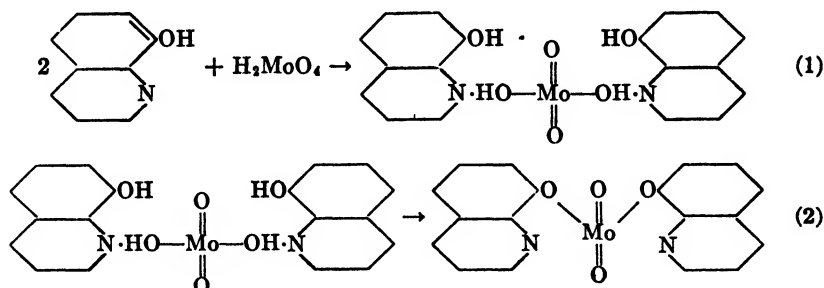
but the other metal acids may react analogously.

According to the view accepted here, the formation of an insoluble binary salt between the basic oxine and the metal acids is the preliminary stage in the production of insoluble oxine esters, which are the final precipitation products of oxine with metal acid-formers.   4-Hydroxybenzothiazole, whose basic character is much less pronounced than that of oxine, obviously forms no insoluble salts by addition reactions with metal acids analogous to the product of reaction scheme (1).   Consequently, the loss of water, analogous to the intramolecular condensation represented by scheme (2), and which is requisite to the production of phenol esters, does not take place.

Although 4-hydroxybenzothiazole possesses a distinct selectivity in contrast to oxine, there is little likelihood at present that it will find any extensive use in analytical work.   It is too difficult to procure.   This fact by no means detracts from the great importance of Erlenmeyer's studies with respect to the chemistry of specific and selective reactions. In all previous comparisons of the analytical behavior of organic reagents containing the same active groups, no particular attention was given to the physicochemical properties of the reagents.   The preceding remarks show that such data may yield valuable indications as to whether certain specific and selective actions will be retained or lost.

Some remarks concerning the evaluation of reagents might be included here.   The practical use of a reagent is often determined by the ease of procuring it or by its cost.   The writer decries any attempt to appraise

[39] A definite oxinate cannot be isolated when molybdenum is precipitated by oxine.   However, the freshly precipitated product behaves considerably like a normal salt with respect to its solubility in acids and alkali hydroxides.   In contrast, the aged product is resistant to acids and bases.   (Unpublished findings of F. FEIGL and C. PADRON.)

the value of a reagent on these terms, although this is often done.[39a] The true value of a reagent is fixed primarily by its specificity, selectivity, and sensitivity. Accordingly, even an expensive reagent, or one that is hard to procure, may be a very valuable analytical tool, if its use saves time and work. Pertinent instances are provided by materials discussed in this chapter:rhodizonic acid; α,α'-phenanthroline; α,α'-dipyridyl; dimethylaminobenzylidenerhodanine. The judgment as to whether a reagent is difficult to procure is often quite subjective. Among organic reagents, it is often possible to develop simpler methods of preparation, and furthermore, it is well known that the cost of making a preparation becomes less if the demand for the product is increased. For instance, dimethylglyoxime is now a common analytical aid, but shortly after it was described as a·reagent for nickel it was marketed in 1 g. lots at a high price. If the value of this excellent reagent had been appraised at that time merely on the basis of the prevailing cost, this factor would undoubtedly have proved a serious handicap to its general use. The efforts to make progress in the chemistry of specific and selective reactions must not be impeded by a prejudice born of the difficulty of preparing new reagents or their cost, nor by the expenditure of time and money required to make adequate tests of their possible applications. The Erlenmeyer reagent, just discussed, is a fine example of the correctness of this viewpoint.

The Behavior of o-Hydroxyaldoximes

Ephraim[40] found that the easily available oxime of salicylaldehyde (I) forms a bright yellow-green copper salt that is difficulty soluble in dilute hydrochloric or acetic acid. It is excellently suited for the qualitative detection and quantitative determination of copper. Salicylaldoxime acts as a monobasic acid, and consequently either the hydrogen atom of the phenolic hydroxyl group (as shown in I) or the hydrogen atom of the likewise acidic oxime group (as shown in II) can be held responsible for the copper salt formation.
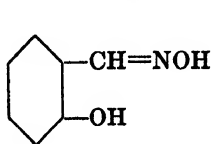
(I)   (II)   (III)
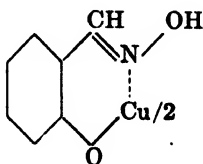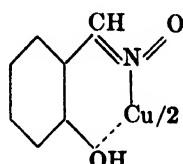
[39a] Compare P. Wenger and R. Duckert, *Helv. Chim. Acta* **24**, 658, 890 (1941).
[40] F. Ephraim, *Ber.* **63**, 1928 (1930).

Ephraim assumed that the phenolic hydrogen is replaced by one equivalent of copper. The correctness of this view was supported by the study of the two isomeric methyl ethers IV and V:

(IV)   and   (V)
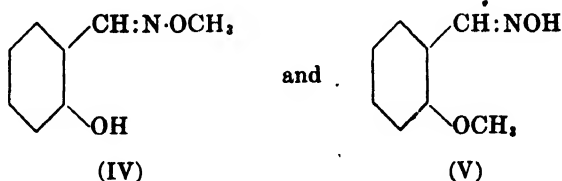
by Feigl and Bondi.[41] Only IV reacts with copper acetate; it produces the dark brown salt[42]
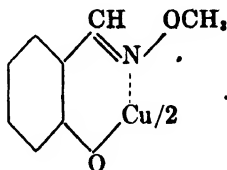
Though, in acetic acid solution, the phenolic OH group of salicylaldoxime is the point of attack by Cu^{++} ions, it is interesting to note that the NOH group can also be forced to participate in salt formation. The reagent then acts as a dibasic acid. Feigl and Bondi (*loc. cit.*) showed that the inner complex Cu-salicylaldoxime on treatment with sodium hydroxide undergoes the following reaction, and produces a normal Cu-salicylaldoximate:
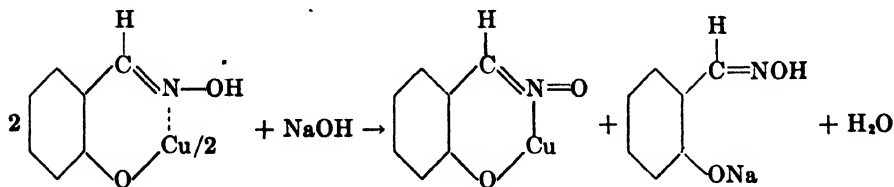
This normal cupric salt is also formed by precipitation when salicylaldoxime reacts with a tartrated copper solution (*e.g.*, Fehling's solution).

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[41] F. FEIGL and A. BONDI, *Ber.* **64**, 2819 (1931).
[42] The precipitation of copper by means of an alcoholic solution of (IV) is quantitative.

The copper salts of the mono- and dibasic salicylaldoxime have practically the same color. Both form almost colorless solutions in ammonia, which indicates that both produce the same unidentified product in this solution process. The activity of salicylaldoxime as a dibasic acid may be taken as a good 'proof of the fact that the oxime group reacts in the

$$=\!N\!\!-\!\!\overset{\displaystyle O}{\|}\!\!-\!\!H$$

=N—H form, as was assumed in the foregoing formula, and not in the =N—OH form. In the latter case, it would be necessary to make the improbable assumption that a 7-membered ring is present in the non-

complex copper salt. In contrast, salification of the =N—H group results in a 6-membered ring just shown.

Ephraim[43] later showed that all of the following compounds, which contain the group that is active in salicylaldoxime, form yellowish copper salts, that are difficulty soluble in acetic acid.
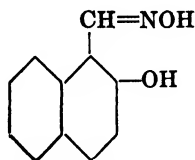
I. 2-Naphthol-1-aldoxime
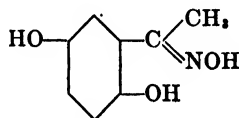
IV. Quinacetophenoneoxime
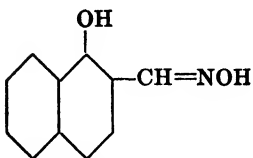
II. 1-Naphthol-2-aldoxime
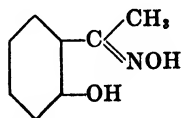
V. o-Hydroxyacetophenoneoxime
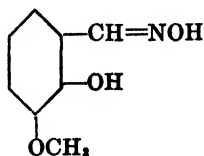
III. Vanillinoxime
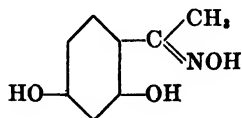
VI. Resacetophenoneoxime

[43] F. EPHRAIM, *Ber.* **64**, 1210 (1931).
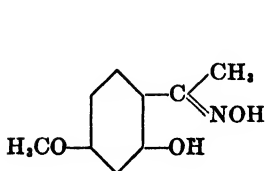
VII. Paeonoloxime
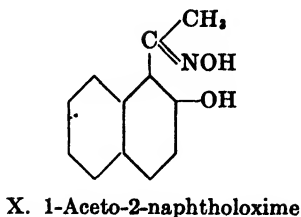
X. 1-Aceto-2-naphtholoxime
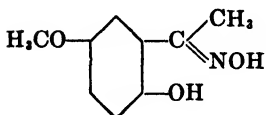
VIII. 5-Methoxyquinacetophenoneoxime
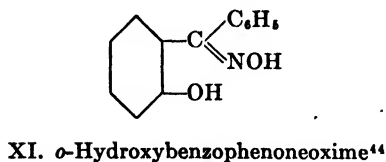
XI. o-Hydroxybenzophenoneoxime[44]
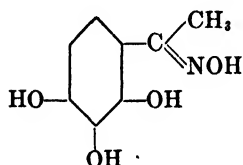
IX. o-Gallacetophenoneoxime
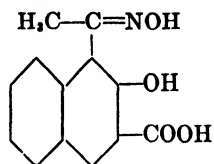
XII. α-1-Acetoneoxime-2-hydroxynaphthoic
acid

The foregoing twelve compounds offer no advantages as analytical reagents over the easily available salicylaldoxime, but they do show that the ability to form copper salts is dependent on the presence of a certain group. Meisenheimer and his coworkers[45] have isolated the α- and β-forms of (XII).

α

β
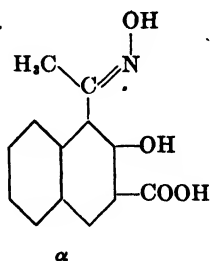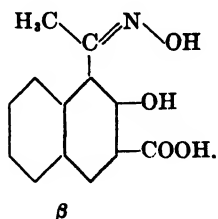
The α-oxime, in which the two OH groups lie farther apart, immediately forms a complex salt by reaction with copper acetate in weak acetic acid solution; in contrast, the β-oxime reacts only insofar as it changes into the α-form. These findings indicate that, in all o-hydroxyaldoximes, the α-form is the active one.

[44] Concerning XI see F. FEIGL and A. BONDI, loc. cit.
[45] J. MEISENHEIMER, W. THEILACKER and O. BEISSWENGER, Ann. 495, 262 (1932).

Salicylaldoxime forms a precipitate solely with copper salts in acetic acid solution. However, Ni^{++}, Co^{++}, Zn^{++}, Cd^{++}, and Pb^{++} ions can be precipitated, in part as colored inner complex salts, from acetate buffered or neutral solutions.[46] Only copper and palladium can be precipitated quantitatively from weak mineral acid solutions.[47] Accordingly, this reagent exhibits a distinct graduated selectivity that is dependent on the pH. Salicylaldoxime in acetic acid solution can even be termed Cu-specific, since the palladium salt is soluble in acetic acid.

It is remarkable that, with the exception of the lead salt, the inner complex salts of salicylaldoxime are soluble in ammonia, some with loss of color. The nature of the resulting compounds has not been clarified.[48] It is also interesting that Co and Ni salicylaldoxinates can be precipitated only from neutral solutions, but once produced, they do not dissolve even in dilute mineral acids. Flagg and Furman[49] made a careful study of the relation of the pH of the solution and the precipitation of metal ions by salicylaldoxime. They found that VO_3^- ions produce a black compound in acid solutions (0.05–1 N) which is in striking contrast to the usual bright colored metal salts of salicylaldoxime. Another interesting finding was that the silver salt of 5-nitrosalicylaldoxime is red, while the introduction of chlorine in the 5-position does not alter the yellow color of silver salicylaldoximate. On the other hand, substitution of NO_2 or Cl invariably produces a change in the color of the soluble ferric salts. Ferric salicylaldoxime is red, the chlorine compound is blue, while the nitro derivative is violet.

There is a similarity between the copper-active group in o-hydroxyaldoximes and the copper-active group in acyloinoximes discussed on p. 266. This is shown by a comparison of the respective groupings

$$\mathrm{HO-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}=NOH} \quad \text{and} \quad \mathrm{HO-\overset{|}{C}H-\overset{|}{C}=NOH}$$
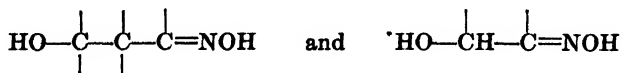
At first glance, it appears that these chains differ solely in the number of their respective C atoms. Therefore, Feigl and Bondi (*loc. cit.*) tested the behavior of the oximes of chloral acetophenone, $CCl_3 \cdot CH(OH) \cdot CH_2 \cdot C(:NOH) \cdot C_6H_5$, and of methyl acetonylcarbinol, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot C(:NOH) \cdot CH_3$, in which the copper-specific group, discovered by Ephraim, is present in an aliphatic system. When treated with copper acetate

[46] Compare F. EPHRAIM, *Ber.* **64**, 1215 (1931).

[47] H. HOLZER, *Z. anal. Chem.* **95**, 392 (1933).

[48] It is not probable that the solution is due to mere addition of NH_3, with production of an ammine salt. It is possible that the acidic NOH group of the inner complex salts reacts with the ammonia forming an ammonium salt of an acid with an inner complex anion (compare pp. 201, 215, 235).

[49] J. F. FLAGG and N. H. FURMAN, *Ind. Eng. Chem., Anal. Ed.* **12**, 529 (1940).

these oximes neither form a precipitate nor undergo any color change that could indicate formation of a salt. It can be concluded that the differences in steric structure and in the acidity relationships due to the aromatic linkage are responsible for the copper-specificity of the o-hydroxyaldoximes.

The Behavior of Hydroxyanthraquinones

Alizarin can serve as a model for the behavior of hydroxyanthraquinones. It was pointed out in the discussion of inner complex compounds that, for various reasons, the dyestuff alizarin belongs to this class of compounds. Consequently, it seems obvious that the ability of alizarin to form inner complexes must also appear in its salts. Möhlau[50] obtained a brown-red precipitate, $Al(C_{14}H_8O_4)_3$, by adding monopotassium alizarinate to a solution of aluminum chloride. Analogous iron and chromium salts have been prepared similarly. The facts that in these salts alizarin functions only as a monobasic acid despite its two o-situated OH groups, and that, as shown especially by the aluminum salt, the color of the salts differs distinctly from that of the alizarinate anion, are indications that these products are inner complex salts with the coordination structure (I). It is noteworthy that these inner complex salts possess an acid character because of their content of three nonsalified OH groups. This is exhibited in their solubility in ammonia; ammonium salts (II) of the respective metal-alizarin acids result.
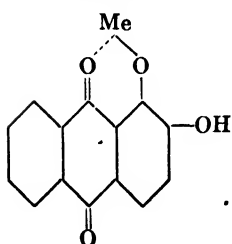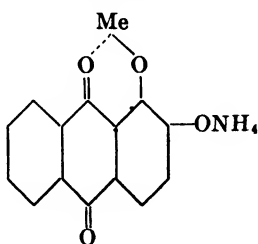
(I)   (II)   Me = ⅓ Al, Fe, Cr

By adding calcium acetate to the ammoniacal solution, Möhlau (loc. cit.) obtained a precipitate of the formula-pure calcium salt of the particular metal-alizarin acid. Consequently, there can be no doubt that alizarin (and other similarly constituted hydroxyanthraquinones) have the ability to bind metal atoms by concurrent action of principal and auxiliary valences. This does not mean, however, that inner complex salts are necessarily formed under the conditions obtaining when hydroxyanthraquinones are used for analytical purposes. They are employed as

[50] R. Möhlau, Ber. **46**, 443 (1913).

reagents usually in ammoniacal or caustic alkaline solutions, and, on adding metal salt solutions, produce colored precipitates which are called color lakes. The first color lake reaction was due to Atack[51] and dealt with the aluminum lake. Subsequently, many such reactions with anthraquinones were described, and found suitable for sensitive tests, frequently even for colorimetric determinations. In the analytical literature, the color lakes are practically always regarded as inner complex salts.[52] However, this notion is not valid, as shown by the mere fact that the products called color lakes contain far less of the organic component than would correspond to an inner complex salt. Nevertheless, such products, which remarkably always form within the existence range of the appropriate metal hydroxide, also may not be regarded as a mixture of hydroxide and inner complex salt. This is shown very definitely by aluminum alizarin lake, which is quite generally considered as the model color lake. This lake does not behave like a mixture of alumina and aluminum alizarinate, because it absolutely lacks the characteristic properties which Möhlau established for aluminum alizarinate: resistance to 1 N hydrochloric acid and solubility in ammonia. The writer[52a] believes that metal color lakes are neither inner complex salts nor mixtures of these with unaltered metal hydroxide. He regards them rather as the products of a chemical adsorption, involving an inner complex binding of acid alizarin dyes to metal atoms of a metal hydroxide surface (see the detailed discussion in Chapter X).

The fact that metal color lakes of hydroxyanthraquinones are not inner complex salts but colored adsorption compounds of variable composition, does not exclude, of course, the possibility that true inner complex salts may not be formed, under suitable conditions, as a phase of their own. In any event, an inner complex binding is involved in both cases; it comes into play because the dye molecule contains an acidic OH group in coordinatable position with respect to an oxygen atom of a CO group. The participation of the CO group is supported by the fact that desoxyalizarin

[51] F. W. ATACK, *J. Soc. Chem. Ind.* **34**, 936 (1945).

[52] Compare J. H. YOE and L. A. SARVER (*op. cit.*), p. 131; H. J. WELCHER (*op. cit.*), Vol. 4, Chapters 14 and 15.

[52a] F. FEIGL and H. W. ZOCHER, unpublished studies.

under comparable conditions, forms no colored aluminum compounds. The behavior of 1-hydroxy- and 2-hydroxyanthraquinone toward ammoniacal copper solutions makes it probable that there is a coordination on the oxygen atom of the CO group,· because only the former completely decolorizes the blue solution, a red-violet precipitate being formed. It is not permissible to conclude merely from the intense color of the aluminum compound that there has been complex linkage, since deepening of color occurs with almost all polyhydroxyanthraquinones when their salts are formed, no matter what the position of the OH groups. A deepening in color, that can be reversed by acids, practically always follows when those hydroxyanthraquinones, that are soluble in alkalies, are dissolved in basic solutions.[53] It has not yet been determined whether the deepening in color is due merely to the formation of the salt of the hydroxyanthraquinone, or whether, in addition, there is a rearrangement that leads to a continuous system of conjugated double bonds:

The excellent agreement of the position of the absorption bands of 2-hydroxy- and 1,2-dihydroxyanthraquinone in alkaline solution, as determined by Meyer and Fischer,[54] argues, in any case, for a decisive effect of the salt formation on the color.

It is notable that 1,2-, 1,3-, 1,4-, 2,3-, 1,5- and 1,7-dihydroxyanthraquinones are taken up from pyridine-ammoniacal solutions by freshly precipitated aluminum hydroxide that has been washed with acetone. Colored materials that are resistant to acetone result, but they become colorless on digestion with hot ammonia. Possibly adsorption phenomena, that precede the formation of a salt, occur here. Salt formation can be assumed with certainty if addition of ammoniacal hydroxyanthraquinone solution to a solution of sodium aluminum tartrate (that is stable to ammonia) produces a precipitate or a color change. This occurs in the following cases:

1,2-dihydroxyanthraquinone, violet to red (ppt. in conc. solutions);

2,3-dihydroxyanthraquinone, blue to red (ppt. in conc. solutions);

[53] Exceptions are 1,7- and 1,8-dihydroxyanthraquinone; they show no color change on solution in alkalies. Compare J. HOUBEN, Das Anthrazen und die Anthrachinone, p. 368. Leipsig, 1929.

[54] R. MEYER and O. FISCHER, Ber. 46, 85 (1913).

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[53] Exceptions are 1,7- and 1,8-dihydroxyanthraquinone; they show no color change on solution in alkalies. Compare J. HOUBEN, Das Anthrazen und die Anthrachinone, p. 368. Leipsig, 1929.

[54] R. MEYER and O. FISCHER, Ber. **46**, 85 (1913).

1,4-dihydroxyanthraquinone, violet precipitate;

1,2,3-trihydroxyanthraquinone, green-brown to violet;

1,2,3-trihydroxybenzophenone, color change.

The behavior of this last compound shows that the presence of even one CO group is sufficient for the formation of a compound with aluminum.

Although the formation of inner complex compounds has not yet been proved definitely for all salts of alizarin, nevertheless, the specific actions of the hydroxyanthraquinones toward the trivalent metals and rare earths deserve full consideration. For example, a saturated solution of 1-hydroxyanthraquinone reacts with beryllium, but not with aluminum ion. Feigl and Krumholz found that this permits the detection of 20γ of beryllium in the presence of 100 times this much aluminum. Similarly, 1,3-dihydroxyanthraquinone reacts, in not too concentrated solution, only with calcium, but not with strontium or barium, forming a fine crystalline precipitate. Quinalizarin
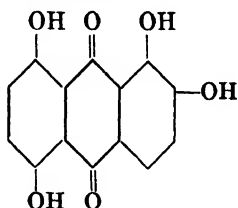
is a sensitive reagent for beryllium and magnesium.[55] Hystazarin (2,3-dihydroxyanthraquinone) is employed for the microchemical determination of the hardness of water.[56]

While aluminum ions react with hydroxyanthraquinones only in neutral or, at most, in weak acetic acid solution, zirconium ions even in mineral acid solution, produce colored (red to blue) precipitates or cause color changes in the hydroxyanthraquinone solution. These effects can be used for the detection of zirconium and fluorine.[57]

1,2-, 1,4-, 2,3-, 2-6-, 2,7-Dihydroxy-, 1,2,4-trihydroxy- and 1,4,5,8-tetrahydroxyanthraquinone, in alcohol solution, give colored precipitates with mineral acid solutions of zirconium salts. The two monohydroxy- as well as 1,3- and 1,5-dihydroxyanthraquinones show no reaction and tint only freshly precipitated zirconium hydroxide.[58]

An argument in favor of compound formation is the fact that when zirconium solutions are treated with alizarin, the precipitate is violet if the zirconium is in excess and red-brown if the alizarin predominates.

[55] F. Feigl, Spot Tests, pp. 148, 172.

[56] F. Feigl, Mikrochemie 7, 8 (1929).

[57] Compare F. Feigl, Spot Tests, pp. 154, 202.

[58] E. Rajmann, Dissertation, Vienna, 1932.

This color shift occurs approximately at a molar ratio of 2 Zr:1 alizarin. The supernatant liquid contains free alizarin only if this ratio is exceeded. On the other hand, thorough washing with organic solvents frequently removes a large part of the alizarin contained in the precipitates. This system seems to represent an intermediate stage between true compounds and loose adsorption complexes. The formation of the latter in acid solution is not excluded, because zirconium salts are hydrolyzed considerably even under these circumstances, and the solutions contain sufficient suspended or colloidal zirconium hydroxide or basic zirconium salt to hold the dyestuff by adsorption.[59]

The color change exhibited by numerous o-hydroxyanthraquinones in concentrated sulfuric acid solution on the addition of boric acid can be used for the detection of the latter.[60] The change probably is the result of the formation of inner complex boron-hydroxyanthraquinone compounds, whose constitution is analogous·to those of the boroacetic acid compounds (see p. 47).

The foregoing examples indicate the important fact that alizarin and similar compounds can act as color reagents in acid as well as in alkaline solution. Further intensive study of the behavior of the numerous hydroxyanthraquinones can be expected to bring to light new and selective reactions that will be useful to the analyst.

The Selective Action of Dicyandiamidine (Guanyl Urea)

Grossmann[61] recommended dicyandiamidine (guanyl urea) as a reagent for copper and nickel. It was among the earliest organic reagents with selective action. Although it has now been largely supplanted by other reagents for these metals, it deserves consideration in the present discussion of atomic groupings and selective action, and also as a complex former.

Dicyandiamidine is a strong, monoacid, water-soluble base, whose salts with mineral acid (I) dissolve readily in water without undergoing hydrolysis. Its yellow insoluble salts with chloroplatinic acid, chloro-

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[59] F. PAVELKA and F. HEISNAR [Kolloid-Z. **66**, 340 (1934)] showed that the colloidal dispersion of the substrate influences its capacity for taking up the color. They found that a weak acid solution of the dye gallocyanine is changed from wine-red by Th-, Ce^{III}-, Fe^{III}-, Sb^{III}-, Bi- and Sn^{IV}-salts, and also by MoO$_3$, WO$_3$ and SiO$_2$. All of these compounds are hydrolyzed in aqueous solutions, and the common cause of the similar color reaction may well be the colloidal dispersion of the hydrolysis products.

[60] F. FEIGL and P. KRUMHOLZ, Mikrochemie, Pregl Festschrift, p. 77, 1929; F. FEIGL, Spot Tests, p. 257.

[61] H. GROSSMANN and B. SCHUECK, Ber. **39**, 3356 (1906); H. GROSSMANN and W. HEILBORN, Ber. **41**, 1878 (1908); H. GROSSMANN and J. MANNHEIM, Chem. Zig. **42**, 17 (1918).

auric acid, picric acid, and phosphotungstic acid have been described; phosphomolybdic acid is likewise precipitated by this reagent. The behavior of dicyandiamidine is thus analogous to that of other polyatomic organic bases. Far more interesting, however, is the fact that this base can function as a monobasic acid in alkaline solution, and that it then forms stable water-insoluble inner complex salts with certain metals. Some of these products are even stable against ammonia. The author accepts the postulate of Yoe and Sarver[62] that the amphoteric behavior of dicyandiamidine is due to an enolization of the CO group to a COH group. Starting with the hydrochloride of the base (I), this enolization, involving the formation of an alkali salt (II), can be represented:

$$
\begin{array}{ccc}
\underset{\substack{\nearrow \\ HN=C \\ \searrow \\ NH-CO-NH_2 }}{NH_2 \cdot HCl}
& + 2NaOH \rightarrow &
\underset{\substack{\nearrow \\ HN=C \\ \searrow \\ NH-C=NH }}{\overset{NH_2}{}\ \ ONa}
& + NaCl + 2H_2O
\end{array}
$$

$$
\begin{array}{cc}
\text{(I)} & \text{(II)}\\
\text{Salt of the baso-form} & \text{Salt of the aci-form}
\end{array}
$$
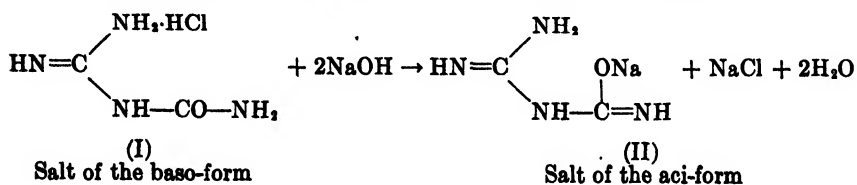
The reaction can be reversed by hydrochloric acid. This is the only known example, among organic reagents, of the rearrangement of a true salt of a base into the alkali salt of an acid that is capable of forming heavy metal salts. Other compounds can be cited in which a salt-formation is assumed to result from a baso-aci equilibrium of tautomeric forms of the particular reagent. However, in all other cases, the basic character of the "baso-form" is exceedingly weak and, in contrast to dicyandiamidine, salt-formations of the baso-forms with acids cannot be detected. The amphoteric function of dicyandiamidine is also not comparable with the amphoteric function of oxine (see p. 182). The latter owes its amphoteric behavior to the possession of both an acidic phenolic OH group and a basic cyclic pyridine nitrogen atom. Dicyandiamidine, on the contrary, is amphoteric because of a shift of a basic hydrogen atom[63] with the consequent development of an enolic OH group.

The heavy metal salts of dicyandiamidine are produced by treating neutral, tartrated solutions of the respective metal salts with the sulfate

[62] J. H. Yoe and L. A. Sarver, Organic Analytical Reagents, p. 127. New York, 1940.

[63] The possibility that the free base dicyandiamidine may itself be regarded as the inner (ammonium) salt of the aci-form is merely mentioned here. This postulation as an ammonium salt: H_2N——O is supported by the insolubility

$$
\underset{\substack{| \\ H }}{HN=C-N-C=NH}
$$
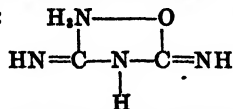
of the base in ether and other organic liquids, which, in general, are excellent solvents for organic bases.

of the reagent, and then adding an alkali hydroxide. The precipitation can also be accomplished from alkaline solutions masked with tartrate, a fact which demonstrates the extremely low solubility of the metal salts of this precipitant. This method was used to precipitate the copper (pink), nickel (orange-yellow), silver (white), and palladium (yellow) salts. The copper and nickel salts do not dissolve in ammonia, whereas the silver and the palladium precipitates are soluble. The metal salts of dicyandiamidine can be represented by either of the coordination formulas (I) or (II):

$$
\begin{array}{cc}
\underset{\text{(I)}}{\underset{\text{H}}{\underset{|}{\text{N}}}-\text{C}=\text{NH}}
\overset{\overset{\text{H}_2}{\text{N}}\cdots\overset{\cdot}{\text{Me}}}{\text{HN}=\text{C}} \diagdown\text{O} &
\overset{\overset{\text{H}}{\text{N}}\cdots\text{Me}}{\text{H}_2\text{N}-\text{C}}\diagdown\text{O}
\end{array}
\qquad \text{(Me} = \tfrac{1}{2}\text{Cu, Ni, Pd or 1 Ag)}
$$

(I)   (II)
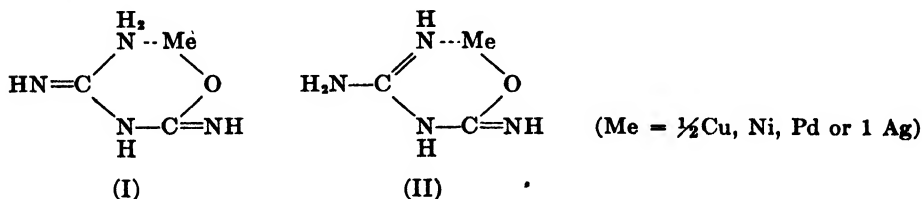
A definite decision between these structures cannot be made at present, although (I) seems to be the more likely. The inner complex salts of dicyandiamidine are not soluble in organic liquids. This characteristic probably is due to the presence of basic groups in the inner complex salt, and accordingly, the solubility rule governing such compounds (see p. 409) operates.

The action of mercuric salts toward dicyandiamidine is noteworthy. Addition of the sulfate of the reagent to neutral mercuric solutions, followed by alkalization, produces a white precipitate. Even Nessler's solution, which contains the complex $[\text{HgI}_4]^{--}$ ion, reacts in this way. Mercuric oxide, unlike $\text{CuO}\cdot x\text{H}_2\text{O}$ and $\text{NiO}\cdot x\text{H}_2\text{O}$, does not react with an alkaline solution of dicyandiamidine.

Its behavior entitles dicyandiamidine to be regarded as a selective reagent in the group of ammine-forming metal ions: (Pd^{++}, Ag^+, Cu^{++}, Co^{++}, Ni^{++}, Zn^{++}). Only copper and nickel are precipitated from ammoniacal solutions, provided any cobalt is previously converted into a trivalent ammine salt. If cobaltous solutions are treated with dicyandiamidine and alkali, the precipitate consists entirely of Co(OH)_2. Hence, cobalt and nickel exhibit no analogy in their behavior toward this reagent.

The analytical employment of derivatives of dicyandiamidine has not yet been tested, because no directions for their preparation has been published.[64] It is entirely possible that the replacement of hydrogen

[64] E. BAUMANN, *Ber.* **7**, 446, 1766 (1874), has described a method for preparing dicyandiamidine, namely, condensation of guanidine and urea, with loss of ammonia. This probably can be readily modified to produce alkyl and aryl derivatives of dicyandiamidine.

in the NH_2 and NH groups by aromatic and aliphatic radicals will result in color effects and modifications of the salt-forming capabilities. The sulfur homolog (guanylthiourea) is known.[65] A study of its analytical behavior would certainly be of interest.

The Thallium-Specific Group —CO—CH₂—CO— (in the Presence of Carbon Disulfide)

The union, in indifferent solvents, of carbon disulfide and thallium acetylacetonate H_3C—(OTl)=CH—CO—CH_3, produces an orange-red precipitate or a yellow coloration. According to Kurowski,[66] this permits the detection of 1 g. CS_2 in a liter of benzene. A study[67] of the behavior of numerous other diketones toward thallium carbonate and carbon disulfide, or of thallium enolates of diketones with carbon disulfide, in indifferent media, has shown that colored (red to yellow) compounds are produced only with 1,3 diketones containing the group —CO—CH₂—CO—. The radicals attached to this group are without effect, but compounds containing thallium do not form if organic radicals have replaced some or all of the hydrogen atoms of the methylene group, or the oxygen atoms of the keto groups.

The compounds of the thallium enolates with carbon disulfide are readily available. They are stable to dilute acids and bases. Two atoms of thallium, one equivalent of the diketone, and one molecule of carbon disulfide are present in every case.

The loss of carbon disulfide, on treatment with acids, supports the coordination formula:[68]
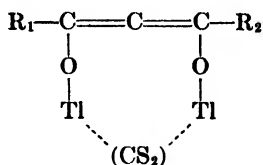
[65] B. RATHKE, *Ber.* **11**, 962 (1878).

[66] E. KUROWSKI, *Ber.* **43**, 1079 (1910).

[67] F. FEIGL and E. BÄCKER, *Monatsh.* **49**, 401 (1928).

[68] The constitution of the colored thallium compounds formed by the action of CS_2 on thallium enolates might also be represented:

$$R_1C(OTl)\!:\!C\!\cdot\!COR_2 \qquad \text{or} \qquad R_1C(OTl)\!:\!CR_2$$
$$\text{CSSTl} \qquad\qquad\qquad \text{OCSSTl}$$
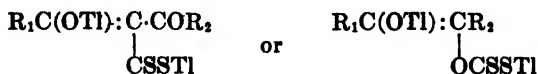
The objection to these formulas is that such derivatives of dithiocarbonic acid ought to form salts at their SH groups with other metals also, particularly with those that combine with sulfur. This is not the case.

This assumption of the double enolization of the methylene group between the CO groups agrees with the finding that the formation of dithallium-carbon disulfide compounds requires the presence of the intact —CO—CH$_2$—CO— group. This group can,.therefore, be considered as specific for thallium in the presence of carbon disulfide. The test has not been used analytically because the reaction with thallium could not be made sufficiently sensitive, but its improvement is not impossible.

The available findings show particularly that in the case of ketones, which form only mono-enol salts with thallium (and other metals), the production of di-enolates is forced by the formation of complex salts. No analogous cases of this are known.[69] This is a further example of the stabilization of abnormal types of compounds by complex formation (see p. 30).

The Behavior of the Group —CO—C(:NOH)— *in Aliphatic Chains*

The group —CO—C(:NOH)—, in open aliphatic chains, that can be produced by the monoximation of a —CO—CO— group or by the isonitrosation of a —CO—CH$_2$— group, shows a characteristic behavior toward ferrous salts in weakly alkaline or acetate-buffered solutions. Whitely[70] was the first to observe, by means of isonitrosoacetone and numerous other analogous compounds, that materials containing this group in open chains react with ferrous sulfate to produce blue compounds. These products are more or less soluble in water, and all of them form blue solutions in organic liquids. This extremely sensitive "iron blue reaction," which can be used for the detection and determination of ferrous iron, is discussed on p. 212. Feigl and his collaborators[71] tested the action of compounds containing the —CO—C(:NOH)— group in aliphatic chains. They found certain regularities, which are interesting from the standpoint of general knowledge of group actions. The results are summarized in Table III.

A study of these findings reveals that the presence of an enolizable CO-group adjacent to a —C(:NOH)— group is essential for the occurrence of the iron blue reaction. This is shown by a comparison of isonitrosoacetophenone (11) and chloroisonitrosoacetophenone (12). There is no possibility of enolization in (12), and accordingly it is wholly unreactive toward ferrous salts. The nècessity of an enolization is supported by the finding that when the hydrogen atoms of the methyl group of isonitrosoacetoacetic ester (6) are successively replaced by

---

[69] Compare K. v. AUWERS, *Ber.* **66**, 959 (1933).

[70] M. A. WHITELY, *J. Chem. Soc.* **83**, 44 (1903).

[71] F. FEIGL, *Oesterr. Chem. Ztg.* **26**, 85 (1923); see also F. RAPPAPORT, Dissertation, Vienna, 1923; and S. TAUBES, Dissertation, Vienna, 1924.

TABLE III

No.	Compound*	Keto form	Enol form	Color reaction with Fe++
1	I-acetone	$CH_3 \cdot CO \cdot CH(:NOH)$	$CH_3 \cdot C(OH):C(:NOH)$	Blue
2	I-acetone methyl ether	$CH_3 \cdot CO \cdot CH(:NOCH_3)$	$CH_3 \cdot C(OH):C(:NOCH_3)$	Blue
3	Di-I-acetone	$CH(:NOH) \cdot CO \cdot CH(:NOH)$	$CH(:NOH) \cdot C(OH) \cdot C(:NOH)$	Blue
4	I-acetylacetone	$CH_3 \cdot CO \cdot C(:NOH) \cdot CO \cdot CH_3$	$CH_3 \cdot CO \cdot C(:NOH) \cdot C(OH):CH_3$	Blue
5	I-methylethylketone	$CH_3 \cdot CO \cdot C(:NOH) \cdot CH_3$	$CH_3:C(OH):C(:NOH) \cdot CH_3$	Blue
6	I-acetoacetic ester	$CH_3 \cdot CO \cdot C(:NOH) \cdot CO_2R$	$CH_3 \cdot C(OH):C(:NOH) \cdot CO_2R$	Blue
7	Brom-I-acetoacetic ester	$CH_2Br \cdot CO \cdot C(:NOH) \cdot CO_2R$	$CHBr:C(OH):C(:NOH) \cdot CO_2R$	Blue
8	Dibrom-I-acetoacetic ester	$CHBr_2 \cdot CO \cdot C(:NOH) \cdot CO_2R$	$CBr_2:C(OH):C(:NOH) \cdot CO_2R$	Red
9	Tribrom-I-acetoacetic ester	Not enolisable		No reaction
10	I-acetonedicarboxylic diester	$RO_2C \cdot CH_2 \cdot CO \cdot C(:NOH) \cdot CO_2R$	$ROOC \cdot CH:C(OH) \cdot C(:NOH) \cdot CO_2R$	Red
11	I-acetophenone	$C_6H_5 \cdot CO \cdot CH(:NOH)$	$C_6H_5 \cdot C(OH):C(:NOH)$	Blue
12	Chlor-I-acetophenone	$C_6H_5 \cdot CO \cdot CCl(:NOH)$	Not enolisable	No reaction
13	I-benzalacetone	$C_6H_5 \cdot CH:CH \cdot CO \cdot CH(:NOH)$	$C_6H_5 \cdot CH:CH \cdot C(OH):C(:NOH)$	Blue
14	I-cinnamalacetone	$C_6H_5 \cdot CH:CH \cdot CH:CH \cdot CO \cdot CH(:NOH)$	$C_6H_5 \cdot CH:CH \cdot CH:CH \cdot C(OH):C(:NOH)$	Green
15	I-benzoylacetone	$C_6H_5 \cdot CO \cdot C(:NOH) \cdot CO \cdot CH_3$	$C_6H_5 \cdot CO \cdot C(:NOH) \cdot C(OH):CH_3$	Blue
16	I-benzoylacetic ester	$C_6H_5 \cdot CO \cdot C(:NOH) \cdot COOR$	Not enolisable	No reaction
17	sym. Dibenzalacetoneoxime	$C_6H_5 \cdot CH:CH \cdot C(:NOH) \cdot CH:CH \cdot C_6H_5$	Not enolisable	No reaction
18	I-cyanacetamide	$NC \cdot C(:NOH) \cdot CO \cdot NH_2$	$NC \cdot C(:NOH) \cdot C(OH):NH$	Blue
19	I-cyanacetylurea	$NC \cdot C(:NOH) \cdot CO \cdot NH \cdot CO \cdot NH_2$	$NC \cdot C(:NOH) \cdot C(OH):N \cdot CO \cdot NH_2$	Violet

* I = isonitroso.

bromine, the ability to form a colored ferrous salt is not lost (7,8) until all three hydrogen atoms have been removed (9). Enolization has then become impossible. It is noteworthy that a red, and not a blue, ferrous salt is formed by the dibrominated member (8)· of this series. It is also interesting to note that isonitrosoacetone methyl ether (2) gives an iron blue reaction, despite its lack of a free NOH-group.

If the —CO—C(:NOH) group in these compounds should be considered entirely apart from the radicals on each side of it, there would be no doubt that the acidic NOH group is solely responsible for the occurrence of the iron blue reaction. Since the intense color of the ferrous compounds and their solubility in organic liquids indicate that they are inner complex salts, formulation (I) would seem to be the only suitable representation of the inner complex rings. However, the dependence of the iron blue reaction on the enolization of the CO group, taken together with the positive response of (2),·leads to the conclusion that the salt formation becomes a function of the enolized OH group. In this case, formulation (II) is permissible for the inner complex ring closure.
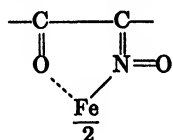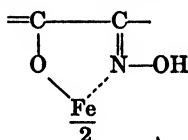
(I)   (II)
(Keto-form)   (Enol-form)

These formulations show that the inner complex ferrous salts, and likewise the parent acidic compounds, are in tautomeric relationship. The ascription of the iron blue reaction to the enolization is correct so far as the compounds contained in the foregoing table are concerned. However, the possibility of enolization cannot be the prerequisite for all cases in which the iron blue reaction is observed. The divergent behavior of the two stereoisomeric benzilmonoximes toward ferrous salts proves this point. α-Benzilmonoxime (III) gives an excellent iron blue reaction, whereas the β-isomer (IV) is completely unreactive:[72]
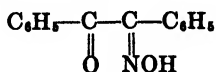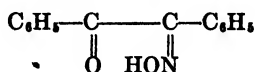
(III)   (IV)

There is no possibility of enolization of the CO group in benzilmonoxime. Accordingly, the occurrence of the iron blue reaction in this case must be determined entirely by the steric position of the NOH group. There-

[72] T. Taylor and E. Ewbank, *J. Chem. Soc.* **129**, 2819 (1926); see also M. A. Whitely, *loc. cit.*

fore, an inner complex ring, as shown in (I), can be the only valid representation of an inner complex ferrous salt of benzilmonoxime. The behavior of α-benzilmonoxime demonstrates that the possibility of forming inner complex rings, as in (I), should not be excluded in the case of compounds containing an enolizable CO—C(:NOH) group. The influence of enolizable CO groups in the CO—C(:NOH) compounds included in the table may, perhaps, be due to their forcing the NOH group to assume a spatial position similar to that in α-benzilmonoxime. Therefore, the structure of the inner complex ferrous salts produced in the iron blue reaction cannot be definitely stated at present. The iron blue reaction was discussed at this point on the assumption that enolic OH groups play a part in the formation of these salts. Should it turn out that the NOH group is the salt-forming group in the compounds considered here, then the iron blue reagents should have been taken up in that section of this chapter, where such activity of this group is stressed.[73]

Representative compounds containing enolizable CO—C(:NOH) groups have been found to be sensitive color reagents for ferrous iron. Kröhnke[74] showed that extraction of ferrous solutions with chloroform solutions of isonitrosoacetophenone (11), after addition of ammonia or disodium phosphate, produces a blue color in the chloroform, with as little as 0.03 mg. Fe^{++}/liter. Dubsky and Kuras[75] used water-soluble diisonitrosoacetone (3) as a reagent for iron. Küster[76] pointed out that 0.0075% ferrous sulfate solution still gives a positive reaction with isonitrosoacetylacetone (4).

However, the iron blue reaction does not have a particularly high analytical value, because it must compete with quite a few other sensitive tests for iron. Furthermore, Kröhnke (*loc. cit.*) and likewise Taylor and Ewbank[77] found that the —CO—C(:NOH) group is not specific for

[73] Two facts may be adduced here against an enolic salt as shown in (II) and in favor of an oxime (keto) salt as represented by (I). The isonitroso compounds discussed in this section manifest no reactivity toward ferric salts. Enolic compounds, which are closely related to the phenols, give red colorations with ferric salts. Furthermore, the excellent solubility in chloroform of the blue inner complex ferrous salts argues against the presence of a free, unsalified NOH group, as shown by (II). Insoluble inner complex metal compounds that still contain an unsalified acid or basic group are usually insoluble in organic liquids (see p. 409). On the other hand, compounds of this kind, from which such unsalified groups are absent, are quite soluble in organic liquids. An application of this rule to the present case indicates that the iron blue reaction produces inner complex ferrous salts with inner complex rings as shown in (I).

[74] E. KRÖHNKE, *Ber.* **60**, 527 (1927).

[75] J. DUBSKY and M. KURAS, *Chem. Abstracts* **24**, 801 (1930); **26**, 2943 (1932).

[76] W. KÜSTER, *Z. physik. Chem.* **155**, 157 (1926).

[77] T. TAYLOR and E. EWBANK, *J. Chem. Soc.* **129**, 2818 (1926).

iron. The following metal ions on treatment with isonitrosoaceto-phenone give colored water-insoluble precipitates, which produce colored solutions in chloroform:

Cobalt	red-yellow	Cadmium	yellow
Nickel	brown	Mercury	yellow
Copper	brown	Lead	red-yellow
Zinc	yellow		

The analytical use of the salts of isonitrosoacetophenone with metals other than iron has not been studied. The cobalt salt is remarkably stable toward acetic acid, in contrast to the nickel salt, which is easily decomposed. Kröhnke, and likewise Taylor and Ewbank, deduce from the analytical data that this product is an inner complex salt of trivalent cobalt, with the —NOH as the acidic group. No decision has been reached as to whether this formulation is correct, or whether the enoliza-tion of the CO group plays a part in this case also. A study, from this standpoint, of the compounds included in the Table would be interesting. The assumption that the NOH group is the active agent is supported by the facts that the cobalt is trivalent, the compound is highly colored, and soluble in organic liquids. These characteristics are strikingly similar to those displayed by the cobaltic salts of isonitrosophenols and -naph-thols. In these latter compounds, after a tautomeric rearrangement, the —CO—C(:NOH) group is located in an aromatic ring. The salt-forming activity of the NOH group in compounds of this type seems to be well established (see p. 255).

The Zirconium-Specific Action of Mandelic Acid

Until recently it seemed that the OH group of the carboxyl group in monocarboxylic acids could not be expected to exhibit selective salt-formation. It appeared particularly very unlikely that organic car-boxylic acids would give rise to salts that would be stable against the action of mineral acids. Consequently, the finding of Kumins[77a] is par-ticularly interesting. He found that the water solution of mandelic acid (phenylglycolic acid) quantitatively precipitates formula-pure zirconium tetramandelate from mineral acid solutions of zirconium salts. The precipitation occurs even from solutions that contain SO_4^{--} ions, in which stable complex $[Zr(SO_4)_3]^{--}$ ions are present. The latter ordinarily pre-vent the precipitation of zirconium from acid solutions. This extraordi-nary behavior indicates that zirconium mandelate is quite insoluble and that only a minute Zr^{++++} ion concentration suffices to exceed the solu-

[77a] C. A. KUMINS, *Anal. Chem.* **19**, 376 (1947).

bility product of this mandelate precipitate. The precipitating action appears to be specific; Fe, Al, Cr, Ti, Sn, Bi, Th, Te, Cu, Cd, vanadate, and alkaline earth ions do not interfere. (Information concerning the behavior of La, In, Sm, Ga, and Ge ions is not available.) The precipitation of zirconium mandelate and its ignition to ZrO_2 provides a method for the quantitative determination of this element and for its separation from the metals just listed.

It is extremely probable that the specific precipitating action of mandelic acid is due to a double binding of the zirconium in the salt, *i.e.*, by a principal valence bond to the carboxyl group and by an auxiliary bond to the neighboring alcoholic OH group. Accordingly, the inner complex salt structure (II) seems to be logical. (In this case, the hydroxyphenylacetic acids (Ia) which are isomeric with mandelic acid (I) will have no analogous precipitating action.)

$$C_6H_5—CH(OH)—COOH$$
$$(I)$$

$$C_6H_4(OH)—CH_2—COOH$$
$$(Ia)$$

$$C_6H_5—CH——C=O$$
$$HO \quad O$$
$$Zr/4$$
$$(II)$$
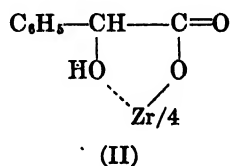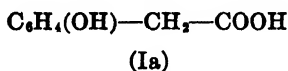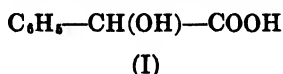
The coordination formula (II) would stipulate for zirconium the coordination number 8, which in general is quite rare. However, it is possible that only two mandelate radicals are bound coordinatively and two others bound normally. Under such circumstances, the zirconium would have the quite common coordination number 6. Information as to which coordination number obtains could be secured by a closer study of Kumin's remarkable discovery of the behavior of zirconium mandelate toward alkali hydroxide and ammonia. Alkali hydroxide causes solution of the salt and precipitation of zirconium hydroxide follows immediately. In contrast, ammonia dissolves the salt without subsequent precipitation of the hydroxide. This behavior testifies to the presence of acidic OH groups in zirconium mandelate, and also shows that soluble ammonium salts are formed. An enhanced acidity of the naturally weakly acidic alcoholic OH group of mandelic acid becomes understandable through the coordination of the zirconium on the oxygen atom of an OH group as shown in (II). This loosens the binding of the hydrogen atom and makes the latter more mobile; *i.e.*, more acidic. Acidic OH groups in zirconium mandelate signify that this inner complex salt has the character of an acid toward alkali. An analogous behavior exhibited by the inner complex palladium dimethylglyoximate is discussed on p. 276. The latter material is soluble in alkali hydroxide; in fact, stable salts of the inner complex palladium dimethylglyoximate can be isolated.

In view of the acidic character of the water-insoluble zirconium mandelate, it, as well as the water-soluble ammonium salt, can be assigned the following formulas of an acid and of a salt with inner complex anions:

$$
\text{H} \left[\begin{array}{c} \text{C}_6\text{H}_5\text{·CH}\text{——}\text{CO} \\ \text{O} \quad\quad \text{O} \\ \text{Zr} \\ \overline{4} \end{array} \right] \qquad \text{NH}_4 \left[\begin{array}{c} \text{C}_6\text{H}_5\text{·CH}\text{——}\text{CO} \\ \text{O} \quad\quad \text{O} \\ \text{Zr} \\ \overline{4} \end{array} \right]
$$
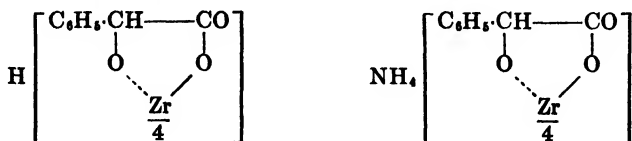
If salts of zirconium mandelic acid should be isolated, their composition will reveal whether two or four mandelate radicals are linked in an inner complex manner to the zirconium. In the first case, 4 hydrogen atoms could be replaced by equivalents of base, while only two hydrogens could be replaced in the second case. The formation of zirconyl salts with two coordinated molecules of ammonia is not excluded among these possibilities, but it is less likely. The elucidation of the process that occurs when zirconium mandelate dissolves in ammonia, together with the analogous behavior of Pd^- dimethylglyoximate is of great interest for a knowledge of the structure of certain types of inner complex salts. In addition, the ammonia-solubility of the mandelate is very remarkable from the analytical standpoint, since the precipitability of zirconium with mandelic acid and the solubility in ammonia shows that mandelic acid functions in one instance as a precipitant and in the other as a masking agent. Should it turn out that the action as a masking agent is just as specific as the precipitating action, further analytical applications can be foreseen.

The zirconium-binding group $CH(OH)\text{·}COOH$ contained in mandelic acid is also present in glycolic acid $H\text{·}CH(OH)COOH$. Accordingly, the latter can be expected to behave analogously toward zirconium, but in a less pronounced fashion since the weighting effect of the phenyl group is absent. Furthermore, it is probable that substitutions in the phenyl group of mandelic acid, and likewise substitution of the naphthyl $(C_{10}H_7)$ for the phenyl (C_6H_5) group would not alter the zirconium-specificity and could lead to new zirconium reagents.

BEHAVIOR OF α- AND o-AMINOCARBOXYLIC ACIDS

There are various reasons why α- and o-aminocarboxylic acids should be of interest and therefore receive special attention in any discussion of the chemistry of specific, selective, and sensitive reactions. The literature dealing with the analytical behavior of these acids provides the best illustration of the following facts: (1) the use of organic reagents has only recently received increased and widespread attention; (2) the search

for organic reagents has been greatly facilitated by adopting the guiding principle serving as the heart of this chapter, namely, that certain groups in organic compounds exhibit definite activities.[77b] Furthermore, the behavior of salts of aminocarboxylic acids demonstrates that it is necessary to proceed more critically than formerly when characterizing inner complex salts.

All α- and o-aminocarboxylic acids contain an atomic group that is characterized by the presence of a coordinatable nitrogen atom so situated with respect to an acidic hydrogen atom of the carboxyl group that 5- or 6-membered inner complex rings can result when the hydrogen is replaced by a metal or radical. The first examples of compounds of this type were the cupric and cobaltic compounds of aminoacetic acid. They were described in 1904 by H. Ley in a paper that is one of the milestones in the progress of the chemistry of complex compounds. In fact, the behavior of these salts led to the coining of the now common designation "inner complex salt." If the principle of analytical group action in organic compounds had been known then or shortly thereafter, attention would doubtless have been turned to homologous amino acids, whose existence and preparation were known. This did not happen. Similarly, investigations of the analytical behavior of other aminocarboxylic acids were not initiated when 9 years later, P. A. Kober and K. Sugiura discovered that α-amino-n-caproic acid is a precipitant for divalent copper.

[77b] Appropriate remarks are included in the theoretical part of the writer's *Spot Test Analysis* (1st. ed., 1930). These were preceded by published articles and doctoral theses with the sub-title "Contributions to the Relations between Atomic Groupings and Specific Affinity." This topic was considered by the writer in numerous lectures and, at the request of the editorial board of *Industrial and Engineering Chemistry*, the first comprehensive treatment of organic reagents, in English, was published [F. FEIGL, *Ind. Eng. Chem., Anal. Ed.* **8**, 401 (1936)]. These efforts admittedly have resulted in the development of a new field of research in analytical chemistry [see, for instance, H. H. WILLARD, *Ind. Eng. Chem., Anal. Ed.* **2**, 202 (1930)]. However, there is no mention of this movement in the books on organic reagents. This fact is stressed here because in the more recent literature on analytical chemistry it seems to be frequently forgotten that every publication contributes and should contribute to the historical picture of the development of the science. It often happens that the discoverers of fundamentally important facts are given a subordinate position in later publications, sometimes they are not even mentioned. Part of the reason for this partial or total neglect may be due to the fact that studies of the literature are often based on abstracts rather than on the original sources. The writer hopes that he is not the only one who believes that literature references, at best, can only provide a formal appearance of completeness. It is desirable for objective reasons to note also facts of priority. Furthermore, such acknowledgment is an ethical duty, which is part of the noblest tradition of every science: to have respect for all scientific labors and, therefore, proper regard for the efforts and successes of others.

It was not until 1933 that H. Funk and M. Ditt found that anthranilic acid is a precipitant for metal ions, and P. Rây and M. K. Bose showed that quinaldic acid acts similarly. Stemming from these two studies, no less than 52 papers appeared by 1946 dealing with the use of these two reagents for qualitative and quantitative purposes.[77a] The analytical usefulness of anthranilic and quinaldic acids was obviously directly responsible for the series of publications since 1936 regarding the use of other amino acids. These findings will also be discussed in this section.

Since all α- and o-aminocarboxylic acids contain an inner complex-forming group that includes a coordinatable nitrogen atom, it may be expected that they will exhibit a reactivity toward ammine-forming metal ions (Cu^{++}, Cd^{++}, Zn^{++}, etc.). This is actually the case but there is also a reactivity toward metal ions which are not pronounced ammine-formers. As is true of all reactions with acid organic compounds, it is not solely a matter of salt-formation, but rather of the production of salts that can be employed analytically because of their appropriate properties. With a single exception, the formation of water-insoluble salts is interesting in the case of the amino acids. As many of these acids are not more than slightly soluble in water, their water-soluble alkali salts are frequently used as precipitants. The available data show that the precipitating action toward neutral metal salt solutions is far more selective with aliphatic aminocarboxylic acids than with the aromatic acids of this class. Almost all of the precipitates produced by means of amino acids are readily decomposed by mineral acids. An outstanding exception is presented by the cupric salts of aromatic o-aminocarboxylic acids. They can be precipitated and are stable at far lower pH values than all the other metal salts. Alkali hydroxides readily decompose the water-insoluble salts of amino acids. The salts of ammine-forming metal ions, without exception, are soluble in ammonia and cannot be precipitated from solutions which contain ammonium salts. No statements regarding the solubility of inner complex salts of α- and o-aminocaboxylic acids in organic solvents have been published. The writer has observed that the cupric salts are not soluble in chloroform, which is a notably good solvent for inner complex salts. Hence, it may be concluded that neither great stability nor pronounced solubility in organic solvents (compare Chapter VIII) is necessarily a characteristic feature of inner complex salts as is often erroneously assumed.

α-Amino-n-Caproic Acid

This acid (I) is only slightly soluble in water. It forms a grey-green precipitate with cupric ions. This action was first observed by Kober

[77a] Compare F. J. WELCHER, Organic Analytical Reagents, Vol. 2, pp. 202, 218, Van Nostrand, New York, 1947.

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and Sugiura[77d] in the course of studies on the reaction of copper hydroxide with amino acids, polypeptides, *etc.* They proved that precipitation could be obtained, not only from solutions of copper salts of other amino acids (with the exception of histidine), but also from alkaline copper solutions masked with tartrate or citrate. In view of its genetic relations to copper glycinate (III), there can be no doubt that the copper salt of α-amino-*n*-caproic acid is an inner complex salt with the coordination formula (II). If the excellent water-solubility of aminoacetic acid and its copper salt is compared with the correspondingly low solubility of aminocaproic acid and its copper salt, it seems logical to ascribe the solubility differences to a weighting effect (see Chapter IX) by the carbon-rich radical superimposed on the inner complex production by the atomic group. The slight solubility of α-amino-*n*-caproic acid is undoubtedly due to this effect. However, the solubility differences of the copper salts certainly cannot be related exclusively to the solubility differences of the acids. It will be pointed out later that aromatic amino acids, which are far more water-soluble than aminocaproic acid, give rise to copper salts, which, in view of their precipitation sensitivities, are obviously much less soluble in water than copper aminocaproate.

$$CH_3(CH_2)_3—CH—COOH \qquad CH_3(CH_2)_3—CH—C{=}O \qquad H_2C{—}{—}C{=}O$$
$$| \qquad\qquad\qquad\qquad | \quad | \qquad\qquad\quad | \quad |$$
$$NH_2 \qquad\qquad\qquad\qquad H_2N \quad O \qquad\quad H_2N \quad O$$
$$\diagdown\diagup \qquad\qquad\quad \diagdown\diagup$$
$$\frac{Cu}{2} \qquad\qquad\quad \frac{Cu}{2}$$

(I)   (II)   (III)
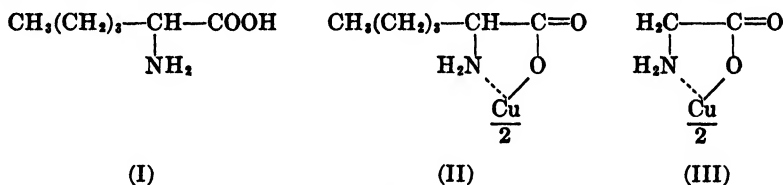
Lyle, Curtman and Marshall[77e] studied intensively the ability of α-amino-*n*-caproic acid to effect precipitation. They found that precipitation still occurs from a copper solution that has been diluted 1:300,000, and that, of the other metal ions, only zinc and mercury react to produce a precipitate. Accordingly, there is a pronounced selectivity even toward ammine-forming ions. Since the aromatic amino acids, which are discussed later, are much less selective in their precipitating action, the aliphatic amino acids certainly merit consideration. Leucine, isomeric with α-amino-*n*-caproic acid, has been shown by Lyle (*loc. cit.*) to act analogously, though with less precipitation sensitivity. Gaptschenko[77f] used the reaction of phenylglycine with copper salts, which had previously been reported by Kober and Sugiura (*loc. cit.*), for the detection of copper in the known absence of gold, silver, and mercury.

[77d] P. A. Kober and K. Sugiura, *J. Am. Chem. Soc.* **35**, 1584 (1913).

[77e] W. G. Lyle, L. J. Curtman and J. T. Marshall, *J. Am. Chem. Soc.* **37**, 1471 (1915).

[77f] M. Gaptschenko, *Chem. Abstracts* **35**, 2810 (1941).

Other aliphatic α-aminocarboxylic acids have not yet been studied with reference to their analytical properties. Such investigations would be interesting because it may be expected that the numerous amino acids, which can be derived from the parent aminoacetic acid through the binding of organic radicals to the inner complex-forming group, would provide a set of interesting comparison materials for the study of group action in organic reagents.

Anthranilic Acid (o-Aminobenzoic Acid)

Funk and his associates[77a] carried out a series of studies on the analytical behavior of anthranilic acid (I). It was found that sodium anthranilate produces crystalline precipitates with many metal ions in neutral or acetic acid solution. The precipitation reactions are still visible in 5 ml. of solution at a dilution of 1:1,000,000. Since anthranilic acid is far more soluble in water than α-amino-n-caproic acid, which was just discussed, it is evident that the water-insolubility of an amino acid is not decisive for the production of insoluble salts. It is therefore likely that the slight solubility of anthranilates of heavy metal is related to the formation of 6-membered inner complex salts as represented by (II).
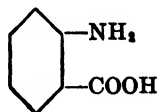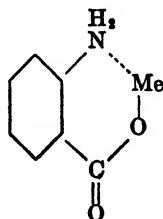
(I)   (II)

The majority of the precipitations of metal anthranilates occur at minimal pH values from 4.7 to 5.2. The copper salt is an exception, it comes down even at pH 2.1.[77b] The analytical importance of the non-selective precipitations of the metal anthranilates resides in the fact that the products are formula-pure, are not affected by drying, contain a low percentage of the metal, and, in addition, offer the possibility of a bromometric procedure through titration of the acid after it is liberated from the salt by treatment with a mineral acid. All these factors have been applied in the quantitative determination of metals.

The silver salt of anthranilic acid will be discussed in particular detail because this inner complex salt has been found to exhibit a mode of

[77a] H. Funk and M. Ditt, Z. anal. Chem. 91, 332 (1933); 93, 241 (1933); H. Funk and F. Römer, ibid. 101, 85 (1935); H. Funk and M. Demmel, ibid. 96, 385 (1934).
[77b] H. Goto, Chem. Abstracts 29, 1029 (1935); 32, 7378 (1938).

reaction that is of basic import in the chemistry of complexes. A classic method of preparing esters is by action of alkyl halides on silver salts of carboxylic acids. Karrer[771] found that silver anthranilate and ethyl iodide produce not only the ethyl ester of anthranilic acid but also N-ethylanthranilic acid. Consequently, both of the following transpositions occur:
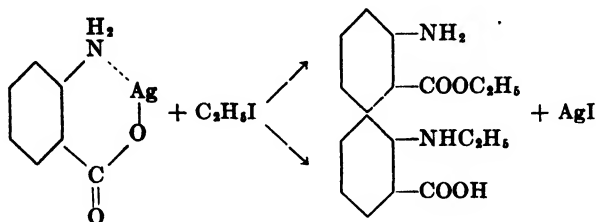
The production of isomers in a reaction as clear-cut as this has been observed with other α- and o-aminocarboxylic acids on treatment with suitable alkyl halides; acetobromoglucose, $BrC_6H_7O_5(OCCH_3)_4$, is the most active. Karrer found further that the inner complex silver salts of α- and o-hydroxycarboxylic acids react analogously with acetobromoglucose to produce concurrently the ester and ether of the respective hydroxy acids. These findings can be taken as definite substantiation of the view that, in inner complex salts, one metal atom is joined to two positions of the same molecule. Karrer suggests that inner complex salts be regarded as an equilibrium mixture of two desmotropic forms, in which the silver atom at times is bound by principal valence forces to one of the two inner complex-forming groups. However, the following concept is likewise worthy of consideration. The coordination of the silver atom on the nitrogen atom of the NH_2-group in amino acids (or on the oxygen atom of the OH-group in hydroxycarboxylic acids) makes the hydrogen atoms more mobile. As a consequence, a reaction may ensue with the halogen atom of an alkyl halide to produce the hydrohalic acid, which then reacts with the salt-like bound silver to produce silver halide. Up to the present, the formation of isomers through the reaction of two different functional groups of an inner complex salt has been observed solely with the silver salts of α- and o-amino- and hydroxycarboxylic acids by reaction with certain (by no means all) alkyl halides. (In view of the pronounced formation-tendency of PdI_2 and TlI, an analogous mode of reaction is not excluded when alkyl iodides react with inner complex salts of palladium or thallium, in which there is coordination on NH_2 or OH groups.) There is no justification, however for the idea that it is characteristic of inner complex salts that both of the func-

[771] P. KARRER, C. NAEGLI and H. WEIDMANN, Helv. Chim. Acta 2, 242 (1919).

tional groups of the inner complex ring react when the ring is ruptured.[77j] Entirely aside from the fact that this is not really true of all alkyl halides, many instances can be cited in which there is no possibility of the simultaneous reaction of two functional groups subsequent to the breaking of inner complex rings. For example, this type of reaction cannot be expected at all when one of the functional groups contains no replaceable hydrogen (e.g., such groups as CO,CS, or —N=N—) which are quite common in inner complex salts. The instance discussed here of the double decomposition of inner complex silver salts indicates, as do the remarks on p. 217 regarding the alleged stability of inner complex salts and their solubility in organic liquids, that unwarranted generalizations must be carefully avoided when characterizing inner complex salts.

Interestingly enough, the isomers of anthranilic acid, namely, m- and p-aminobenzoic acid, likewise give precipitates with copper salts. These precipitation products, which can be used to detect copper,[77k] cannot be inner complex salts since, in these reagents, the amino group is not in a coordinatable position relative to the carboxyl group. Possibly the products are basic salts.

Among the derivatives of anthranilic acid, studies have been made with 3-amino-2-naphthionic acid[77l] and 5-bromo-2-aminobenzoic acid.[77m] Their behavior is analogous to that of anthranilic acid. No study has yet been made to learn whether the precipitates obtained with the substituted anthranilic acids are less soluble than the corresponding metal anthranilates.

Quinaldic Acid (Quinoline-2-Carboxylic Acid)

Rây and his collaborators[77n] were the first to recognize and study the analytical behavior of quinaldic acid (I). It is quite soluble in water. Acetate-buffered solutions of Hg, Pb, Ag, Cu, Cd, Mn, Co, and Ni react with this reagent to form crystalline precipitates of the general formula (II). Amorphous yellow precipitates of varying composition (probably basic salts) result when an alkali quinaldate is added to solutions of

[77j] This generalization is found in F. J. WELCHER, op. cit., Vol. 2, p. 23, with reference to the silver anthranilate-ethyl iodide reaction. Neither the author nor the place of publication of this study is given (see footnote 77b on p. 216).

[77k] E. A. KOCSIS and collaborators, Mikrochemie ver. Mikrochim. Acta 29, 166 (1941).

[77l] R. J. SHENNAN, J. H. SMITH and A. M. WARD, Analyst 61, 395 (1936).

[77m] R. J. SHENNAN, J. Soc. Chem. Ind. 61, 164 (1942).

[77n] P. RÂY and M. K. BOSE, Z. anal. Chem. 95, 400 (1933); P. RÂY and A. K. MAJUMDAR, ibid. 100, 324 (1935); P. RÂY and M. K. DITT, ibid. 115, 265 (1939); P. RÂY and J. GUPTA, Mikrochemie 17, 14 (1935); P. RÂY and T. C. SARKER, ibid. 27, 64 (1934).

Fe, UO$_2$, Al, Cr, Bi, and Ti. The precipitation sensitivity with copper and zinc is very high; 1:20,000,000 and 1:15,000,000, respectively. The marked decrease with cadmium (1:1,500,000) is striking. Perhaps this difference is related to the fact that the cadmium quinaldate is anhydrous, while the copper and zinc salts are highly hydrated. Monohydrates of the latter salts remain if the precipitates are dried at 125°C.; the zinc salt withstands temperatures up to 175°C. This tenacious binding of water, which is not encountered, either with other quinaldates nor with other metal salts of o-aminocarboxylic acids, is rather strange. It demands an explanation since the assumption of the coordination of one H$_2$O molecule on one molecule of Cu (Zn) quinaldate leads to the unlikely coordination number 5. Perhaps drying of the hydrated copper and zinc quinaldates results in the production of basic salts with one molecule of coordinated quinaldic acid. This would correspond to the coordination number 4. Moreover, the possibility of a coordination of water molecules on inner complex salts should not be excluded. The existence of definite hydrates of inner complex metal oxinates (see p. 185) shows clearly that the notion that inner complex salts are coordinatively saturated (see p. 184) is surely not valid in this general form. As is true of almost all aromatic amino acids, the green crystalline copper quinaldate can be successfully precipitated at lower pH values than all other metal quinaldates. This finding can be made the basis of the separation of copper from other metals. Majumdar[77o] made the interesting discovery that the solubility of this copper salt is not identical in acetic and sulfuric acids of equal pH. At pH 2.05, the solubility in acetic acid is about 10 times as great as in sulfuric acid. Consequently, a specific effect of acetic acid is evidenced, and this may be connected with the fact that copper acetate solution exerts a solvent action on copper quinaldate.

(I)   (II)
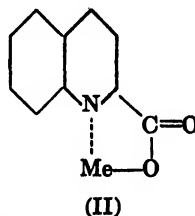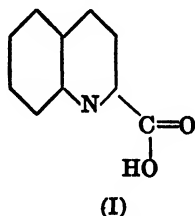
It seems as though the inner complex character is more decidedly marked in the inner complex salts of quinaldic acid than in the salts of all other α- and o-aminocarboxylic acids. This is not shown by a distinctly greater stability at certain pH values, but rather in certain other properties. Thus, cadmium quinaldate can be melted without decom-

77o A. K. MAJUMDAR, Analyst 68, 242 (1943).

position at 150°C., and the zinc salt at 170°C. Furthermore, remarkable color anomalies are shown by certain of these salts. The cobalt salt is the only known colorless cobalt salt. This finding is all the more surprising since it is precisely the cobalt inner complex salts that are noted for depth of color. Nickel quinaldate is reddish white and hence it also is exceptional, since the nickel salts of aminocarboxylic acids are generally greenish yellow.

Neutral ferrous solutions, on treatment at room temperature with alkali quinaldate, produce a dark red, fairly soluble precipitate. On standing, or more rapidly if warmed, this changes to a less soluble blue-violet product. Rây and Bose (*loc. cit.*) assume that the unstable *cis*-form (I) of the iron complex rearranges to a more stable *trans*-form (II):

(I)   (II)
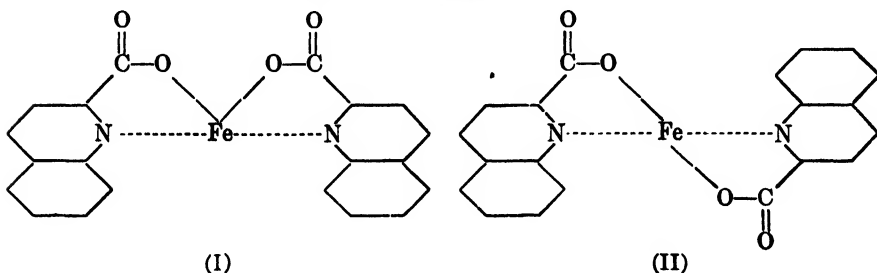
As no other instances of a *cis-trans* isomerism have as yet been observed among inner complex salts of quinaldic acid, nor among salts of other aromatic aminocarboxylic acids, the present writer believes that another interpretation should be considered. The blue-violet product is the only one of the various colored ferrous salts of quinaldic acid that has been isolated in the formula-pure state. It proved to be anhydrous. Therefore, it is possible that the red form is a dihydrate, with the coordination number 6, which is reached quite often in ferrous salts. The color change may thus be due simply to a spontaneous dehydration of the precipitate. Differences in color between hydrated and anhydrous forms of the same material are so common that this possibility simply cannot be disregarded in the present case. (It is pertinent to recall here the dehydration of blue $CuO \cdot xH_2O$ to black $CuO \cdot H_2O$.) Other hitherto unexplained findings can be brought into harmony with the postulate that the red product is an hydrate. Thus, dilute ferrous solutions on treatment with alkali quinaldate yield a pale red coloration, which is stable, and the intensity of which is heightened by the addition of dilute potassium cyanide solution. It appears, therefore, that colloidally dispersed ferrous quinaldate does not undergo a transformation into a *trans*-isomer, nor does it suffer a dehydration. Rather, it is stabilized by potassium cyanide, which is perhaps coordinated. The ferrous quinaldate reaction has a sensitivity

of 1:14,500,000 and can be used in the colorimetric determination of small quantities of iron.

Quinoline-8-Carboxylic Acid

Majumdar[77b] found that quinoline-8-carboxylic acid (I) is a precipitant for Cu^{++}, Cd^{++}, Hg^{++}, Ag^+, and Tl^+ ions. The reagent is quite soluble in water. Its precipitating action with thallium is noteworthy, as other aromatic amino acids do not have this ability. No figures are available regarding its precipitation sensitivities. All these precipitations doubtless involve the formation of inner complex salts, which can be formulated as shown in (II).
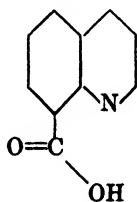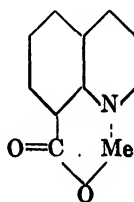
(I)   (II)

Quinoline-8-carboxylic acid is isomeric with quinaldic acid (quinoline-2-carboxylic acid) just discussed. Consequently, the salts of these two monobasic acids must also be isomeric with each other. If the structure of these acids is considered, it becomes clear that a salt-isomerism will exist, which for the present is unique. In one case (quinoline-2-carboxylic acid) 5-membered rings will be present in the inner complex salts, in the other case (quinoline-8-carboxylic acid) 6-membered rings will be present. How this extension of the rings will be reflected in the properties of the respective salts is not known and would be well worth studying. It may be that the precipitating action toward thallium is related to the ring extension and likewise this may be reflected in the fact that ferrous solutions give a red color with quinoline-8-carboxylic acid, in contrast with quinoline-2-carboxylic acid which acts as a precipitant.

The constitutional similarity of quinoline-8-carboxylic acid to o-aminobenzoic acid and to 8-hydroxyquinoline is noteworthy. Whether, this constitutional similarity shows itself in the properties of the salts, and how, is not known. Quinoline-8-carboxylic acid is amphoteric in the same way as 8-hydroxyquinoline is; it is excellently soluble in acids and bases. Since it will probably be found that the acid is readily brominated, there are interesting prospects for analytical applications and also

[77b] A. K. MAJUMDAR, *J. Ind. Chem. Soc.* **18**, 419 (1941).

for studies of group actions.   As yet, quinoline-8-carboxylic acid has been used only for the gravimetric determination of copper, and for separating it from cadmium and zinc.[77a]

Other o-Aminocarboxylic Acids

The activity of derivatives of anthranilic acid was referred to on p. 221.   Lott[77r] used 5-nitroquinaldic acid for an interesting method of determining zinc.   The zinc salt is precipitated from an acetic acid solution, and the precipitate is then dissolved in a hydrochloric acid solution of stannous chloride.   The resulting orange-red product is probably a nitrosoquinaldic acid.   Small quantities of zinc can be determined colorimetrically by this procedure.   Dubsky and Hrdlicka[77s] studied the precipitating action of 1-aminoanthraquinone-2-carboxylic acid.   With the exception of the alkali metals, all other metals form red precipitates.   Accordingly, there is no indication of any selectivity in the action of this amino acid.   Possibly this is connected with a size effect exerted by the large anionic portion of the acid molecule.

ACIDIC SH GROUPS, BOUND TO CARBON ATOMS

The —SH groups of organic compounds invariably possess a more acid character than analogously bound-OH groups. ‘ This is shown, for example, by the fact that the hydrogen atom in primary-SH groups, in contrast to that of primary-OH groups, can be replaced by heavy metals with production of insoluble compounds.   This tendency to form insoluble heavy metal salts is likewise more marked in —SH groups linked to aromatic radicals than in the corresponding hydroxy compounds.   Thioketo groups also play an important part among organic compounds that have interesting analytical action.   They, like the analogous keto groups, can undergo a change into thioenol groups,

$$\underset{\displaystyle CH_2}{\diagdown}C{=}S \rightarrow \underset{\displaystyle -CH}{\diagdown}C{-}SH.$$ The rearrangement is favored by OH⁻ ions,

whereas H⁺ ions stop it.   In many cases, the ability to form salts makes it necessary to assume that solutions of thioketo compounds contain an equilibrium mixture of the thioketo and thioenol forms.   Consequently, such compounds can react in their respective tautomeric forms.   The proximity of atoms that can exhibit coordination ability

[77a] A. K. MAJUMDAR, loc. cit.; compare also J. R. GILBREATH and H. M. HAENDLER, Ind. Eng. Chem., Anal. Ed. 14, 866 (1942).

[77r] W. L. LOTT, Ind. Eng. Chem., Anal. Ed. 10, 335 (1938).

[77s] J. V. DUBSKY and M. HRDLICKA, Mikrochemie 22, 116 (1937).

plays a great role in the selective action of —SH groups, just as it does in the hydroxy compounds. The result may be the formation of inner complex salts, which, by virtue of their color, slight solubility in water, or ready solubility in organic liquids, may be used as the basis of specific or selective tests and determinations. Organic compounds with SH groups often show a remarkable analogy to hydrogen sulfide in their precipitating action. Hence, —SH groups bound to organic radicals clearly demonstrate that they are organic derivatives of hydrogen sulfide. On the other hand, mercapto compounds have a stronger reducing action than H_2S, or S^{--} and SH^- ions. Accordingly, when dealing with mercapto compounds, there is considerable likelihood of redox-reactions which result in the production of stable disulfides of the general formula R—S—S—R. As such disulfides likewise result from autoxidation, mercaptans, as a rule, are unstable reagents.

Selective Actions of 1,2-Mercaptobenzenes

A comparison of phenol, C_6H_5OH, with thiophenol, C_6H_5SH, reveals that the acidic character of the SH group and its ability to form heavy metal salts are more greatly influenced by the negative C_6H_5 group than are the corresponding characteristics of the OH group. This is shown plainly by the fact that precipitates of the respective metal thiophenolates are obtained when thiophenol is added to acidified solutions of salts of heavy metals which have a pronounced affinity for sulfur (Ag, Hg, Pb). The color of the phenyl mercaptides of mercury (colorless), silver and lead (light yellow) obviously does not correspond with that of the respective sulfides. This behavior, which is also observed with nuclear-substituted monothiophenols, alters when a second SH group is introduced into the benzene nucleus in the position that is *ortho* to the first SH group. Cases in point are 4-chloro-1,2-dimercaptobenzene (I) and 4-methyl-1,2-dimercaptobenzene (II). These substituted dimercaptobenzenes, which are readily prepared, produce colored precipitates from acidified solutions with all metal ions that are precipitable by hydrogen sulfide; they also precipitate cobalt and nickel. Clark,[78] who made an extensive study of these reagents, recommends the formation of the red stannous compound as a means of detecting and determining tin. The salts probably have the general structure (III).[79]

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[78] R. E. D. CLARK, *Analyst* **61**, 242 (1936); **62**, 661 (1937).

[79] The possibility should not be excluded that in certain salts there may be an eventual addition of dimercaptan, and possibly also a formation of sulfo salts, especially in the case of lead and mercury. This would be analogous to the production of sulfo salts in precipitations by means of hydrogen sulfide.

(I) is a benzene ring with —SH and —SH groups and Cl.
(II) is a benzene ring with —SH and —SH groups and H_3C.
(III) is a benzene ring with two S atoms bridging to $Me^{II}(\tfrac{2}{3}Me^{III})$, with $(CH_3)Cl$.
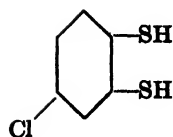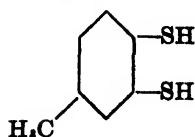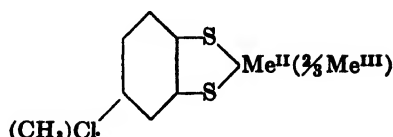
(I)	(II)	(III)

No analytical data regarding the heavy metal salts of (I) and (II) had been available heretofore. The precipitates from solutions containing mineral acids were described:

Ag	yellow	As	pale yellow
Hg	pale yellow	Sb	yellow
Pb	bright yellow	Sn^{II}	magenta red
Bi	brick red	Co	black
Cu	black	Ni	black
Cd	pale yellow	Mo	red

The acid-insolubility and the color quality of the metal dimercaptobenzenes are remarkable. It seems logical to ascribe both of these characteristics to the fact, as shown by (III), that a 5-membered ring results when the salts are formed. In certain cases, there may also be a coordination of metal atoms on unsaturated carbon atoms of the benzene ring. Information on this point could be secured by a study of the behavior of 1,2-dimercaptobenzene and of the fully hydrogenated 1,2-dimercaptohexahydrobenzene.

It is striking that the cobalt and nickel precipitates obtained from acidified solutions are black, which is likewise the color of the sulfides. The latter are not precipitable from mineral acid solutions by hydrogen sulfide, because of the formation of acid-soluble α-forms. However, if the sulfides are precipitated, in their β-forms, from alkaline solutions, they are not soluble in dilute non-oxidizing mineral acids. In other words, once precipitated, CoS and NiS belong to the group of difficultly acid-soluble sulfides (PbS, CuS, CdS, etc.). This membership, which is not revealed when hydrogen sulfide is used, appears clearly if the mercaptobenzenes are employed as precipitants. Similarly, molybdenum is immediately precipitated from acid solutions by the dimercaptobenzenes, whereas a quantitative precipitation with hydrogen sulfide is obtained only if the gas is applied under pressure. Consequently, the 1,2-dimercaptobenzenes (I) and (II) can be considered as general precipitants for those metal ions whose precipitated sulfides are stable toward acids. Although this signifies merely an extension of the precipitating action beyond that attainable with hydrogen sulfide, the mercapto precipitation is nevertheless capable of producing tests, separations, and probably even

quantitative determinations that are not possible with hydrogen sulfide. For example, after removal of the ions that can be precipitated from acidified solutions by hydrogen sulfide, cobalt and nickel may be easily separated from iron, manganese, zinc, and the like. This separation is accomplished by means of a mercapto precipitation and the procedure is much simpler than the usual ammonia-ammonium sulfide precipitation. Furthermore, if a metal salt solution is treated with an excess of caustic alkali, any tin remains in the filtrate from the hydrous oxide precipitate. The stannite (stannate) solution can then be acidified and the tin precipitated by means of a mercaptobenzene. Finally, the characteristic red color of the stannous compound permits its recognition even in the presence of light colored mercaptobenzides produced by other metals. This is of special advantage when it is desired to detect tin in the presence of arsenic and antimony. No detailed quantitative studies of this have been made, nor of the possible relation between the precipitating action of these reagents and pH. Likewise, with the exception of tin, no data are available regarding the attainable precipitation sensitivities. Tin can be precipitated from solutions containing up to 15% of hydrochloric acid, the concentration sensitivity is 1:1,000,000. This far exceeds the sensitivity of the SnS_2 precipitation. The combination of this great precipitation sensitivity and the characteristic red color of the stannous compound makes it possible to secure excellent results in colorimetric determinations of this metal.

The mercaptans (I) and (II) are strong reducing agents; when oxidized they produce the corresponding disulfides. Hence tin never precipitates in the quadrivalent but always in the divalent condition. This is a definite difference from hydrogen sulfide, which exerts no reducing action on stannic salts and throws down SnS_2 from stannic solutions. The instability of brown stannous sulfide is noticeable in contrast to the stability of the red stannous dimercaptobenzenes. This is a reflection of the stabilizing effect of the ring formation shown in (III). The reagent is used in 0.2% alkaline solution, but autoxidation to inactive disulfide soon renders this solution unusable. Hence it is necessary to include thioglycolic acid in the reagent solution, because it is more readily oxidized by the air than (I) or (II). Thioglycolic acid, in an acid medium, also reduces any quadrivalent tin to the reactive stannous condition. It likewise renders inactive numerous other oxidizing agents, such as ferric salts.

Hamence[80] made some remarkable observations on the heavy metal precipitates obtained by treating acidified solutions with dimercaptobenzenes. He found that these products dissolve in ammonia to produce

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[80] J. H. HAMENCE, Analyst 65, 152 (1940).

practically colorless solutions. It is not known what compounds are formed by this procedure. This general solubility and the fact that the black copper compound forms not a blue but a colorless solution argue against the natural assumption that ammonia has been added or intercalated. It is quite likely that solution occurs only when an excess of the reagent is present and this leads to the production of complex compounds of the general formulas (IV) and (V).[81] Additional support for this view is given by (VI). This colorless crystalline compound was obtained[82] by the action of mercuric oxide on alcoholic solutions of the monopotassium salt of dimercaptobenzene:

(IV)   (V)

(VI)
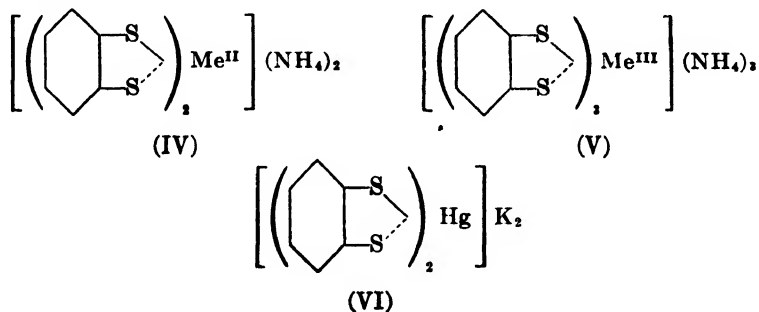
In case solution of heavy metal dimercaptobenzenes in ammonia leads to compounds of the types (IV) and (V), solubility in caustic alkalies can be expected, with formation of the corresponding alkali salts. Such compounds would contain colorless inner complex anions originating from colored principal valence compounds.

Other observations, that have analytical interest, were made by Hamence (*loc. cit.*). Colored precipitates are formed if acidified solutions of molybdates or tungstates are treated with thioglycolic acid and then with a solution of· (I) or (II). The molybdenum precipitate is green, the tungsten compound is light greenish-blue. Both can be extracted from an aqueous suspension by an ether-amyl alcohol mixture, in which they form olive-green and blue solutions, respectively. As little as 0.02 mg. metal in 10 ml. (1:500,000) can be detected in this way. The molybdenum compound forms a blue solution if it is dissolved in ammonia. The tungsten compound, like the other heavy metal dimercaptobenzenes, forms a colorless ammoniacal solution.

There is no information available as to how metal ions (Fe^{++}, Mn^{++}, Zn^{++}, *etc.*), that are not precipitable from acidified solutions by these reagents, will act toward solutions of the alkali salts of these dimercapto-

[81] Substitution in the nucleus is disregarded here.
[82] W. H. MILLS and R. E. D. CLARK, *J. Chem. Soc.* **136**, 175 (1936).

benzenes. Likewise, the platinum metals have not been studied, nor has an investigation been made of the heavy metal precipitates with respect to their solubility in organic liquids. It is probable that the mercaptobenzenes discussed here will be found useful in analytical procedures. In this connection, as well as with regard to the problems presented by the chemistry of complex compounds, it seems clear that the mercaptobenzenes will be among the most interesting of the newly introduced organic reagents.

Selective and Specific Actions of Thioglycolic Acid β-Aminonaphthalide (Thionalid)

The behavior of thioglycolic β-aminonaphthalide (commonly known as thionalid) toward metal ions was extensively studied by Berg and his co-workers.[83] They demonstrated its analytical usefulness as a precipitant in numerous instances. Thionalid, as shown in (I), is both a thioalcohol (mercaptan) and an aromatic amide. It owes its salt-forming abilities to its SH group. Many of its heavy metal salts have been isolated in a form corresponding to the formulas given here. Without exception, they are inner complex salts in which an NH, CO, or an OH group, the latter formed by enolization, provides the coordinative linkage. The production of rings in these salts is clearly evident in (IIa), (IIb), and (IIc) respectively:

(I)

(IIa)

(IIb)

(IIc)
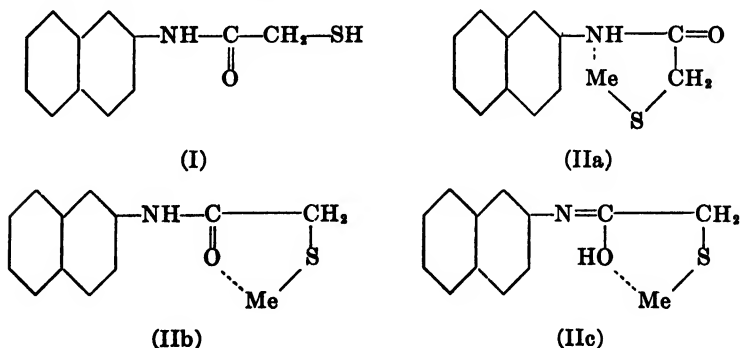
Thionalid is practically insoluble in water, but dissolves easily in the ordinary organic solvents, such as alcohol and acetone. Its ready solubility in glacial acetic acid and its relatively high solubility in water-glacial acetic acid mixtures are remarkable.

[83] R. Berg and W. Roebling, Ber. 68, 403 (1935); Z. angew. Chem. 48, 430, 597 (1935); R. Berg and E. S. Fahrenkamp, Z. anal. Chem. 109, 305 (1937); 112, 162 (1938); R. Berg, E. S. Fahrenkamp and W. Roebling, Mikrochemie, Molisch Festschrift, 1936, p. 42.

This reagent has a marked precipitating action toward the metal ions that are precipitated as sulfides in acid, neutral, or alkaline media. However, there is no strict parallelism with the precipitating action of HS^- and S^{--} ions. For instance, Pb^{++} and Cd^{++} ions, which readily form sulfide precipitates in acid solutions, are not thrown down by thionalid from dilute mineral acid solutions. Furthermore, the two classes of precipitates differ in color. Most of the thionalid precipitates are white to whitish-yellow, although the Pd, Au, Ru[84], Rh[85], Co, and Ni precipitates are yellow-brown to brown.

Table IV shows the high sensitivity of these precipitations and thus indicates the value of the metal thionalid precipitations in qualitative analyses. The inner complex salts come down pure, their metal content is relatively low, and they can be weighed directly in this form. These are great advantages in quantitative work.

TABLE IV

Action of Thionalid

Metal	Concentration limit[a]	Identification limit[a] γ, ml.	Color of complex	Solubility in chloroform
Ag	1:5,000,000	0.2	Yellow	Insoluble
As^{III}	1:100,000,000	0.01	White	Soluble
Au^{III}	1:2,500,000	0.4	Yellowish-brown	Insoluble
Bi	1:10,000,000	0.1	Yellow	Soluble
Cu^{II}	1:10,000,000	0.1	Yellow	Insoluble
Hg^{II}	1:15,000,000	0 06	White	Insoluble
Pb	1:10,000,000	0.1	Yellow	Insoluble
Pd^{II}	1:10,000,000	0.1	Yellow	Soluble
Pt^{II}	1:10,000,000	0.1	Yellow	Soluble
Sb^{III}	1:10,000,000	0.1	White	Soluble
Sn^{II}	1:12,500,000	0.08	White	Insoluble[b]
Sn^{IV}	1:12,500,000	0.08	White	Insoluble[b]
Tl^{I}	1:10,000,000	0.1	Lemon-yellow	Insoluble

[a] The concentration limit and identification limit were determined in 5 ml. of solution to which 0.5 ml. of 2 N mineral acid was added. Only the values for lead and thallium were determined in acetate-buffered or in neutral solution.

[b] Soluble at first, then gradually precipitates.

The color and behavior toward chloroform of a few metal thionalids precipitated from acetate buffered-acetic acid are:

[84] W. D. ROGERS, F. BEAMISCH and D. S. RUSSELL, *Ind. Eng. Chem., Anal. Ed.* **12**, 561 (1940).

[85] H. KIENITZ and L. ROMBOCK, *Z. anal. Chem.* **117**, 241 (1939).

Cadmium	white	soluble
Manganese	white	soluble
Cobalt[II]	brown-red	soluble
Nickel	brown	insoluble

The precipitating action of thionalid is only slightly selective in mineral acid, acetic acid, and neutral solutions. In alkaline media, and with the addition of masking agents, the selectivity can be raised and absolute specificity can be attained in the case of thallium. The following summary reveals the dependence of the precipitating action on the reaction conditions:

Precipitable from mineral acid solution: Cu, Ag, Au, Hg, As, Bi, Pt, Pd, Ro, Rh.

Precipitable from acetic acid or neutral solution: as in (1) also Cd, Pb, Ni, Co, Mn, Tl.

Precipitable from sodium carbonate plus alkali tartrate solution: Cu, Au, Hg, Cd, Tl.

Precipitable from alkali cyanide plus tartrate solution: Au, Tl, Sn, Pb, Sb, Bi.

Precipitable from alkali cyanide plus tartrate plus NaOH solution: Tl. Only alkali tartrate and cyanide have been tested as complex formers in this connection. It is quite possible that other organic complex formers (*e.g.,* sulfosalicylic acid, malonic acid, *etc.*) can enhance the selectivity of the precipitating action of thionalid. Phosphoric acid masks the precipitation of tin by thionalid in mixtures of arsenic, antimony, and tin, but leaves the precipitation of the other two metals unaffected.[36]

Among the compounds that have the same active atomic grouping as thionalid, the N-methylated derivative, $C_{10}H_7N(CH_3)CO \cdot CH_2 \cdot SH$, behaves like the parent compound. This shows that the NH group *per se* is not salt-forming, but only the SH group has this ability. If the naphthyl radical is replaced by phenyl, the precipitating action of the resulting thioglycolic acid anilide is similar, but the sensitivity of the precipitations is definitely less. Consequently, the weighting effect of the naphthyl radical is pronounced (see p. 414). The substitution of anthracyl for naphthyl would doubtless give a further rise in sensitivity. It should be interesting to learn whether the inclusion of chromophoric groups in the thionalid molecule would be reflected in a heightened color of the metal salts.

[36] R. Berg and W. Roebling, *Ber.* **68**, 403 (1935); *Z. angew. Chem.* **48**, 430, 597 (1935).

Since thionalid is a mercaptan, it is not stable toward air.   Hence, it is necessary to use freshly prepared solutions.[87]   The SH group is very readily oxidized; the disulfide $[C_{10}H_7 \cdot NH \cdot CO \cdot CH_2 \cdot S^-]_2$ results.   The latter forms no precipitates with metal ions.   This again indicates that the NH group, which is present in both the parent compound and the disulfide, has no salt-forming ability.   The ease with which the disulfide is formed, makes it impossible to use thionalid directly in the presence of oxidants, even those as weak as ferric ions.   In such cases, it is well to add hydrazine salts as preventive antioxidant agents.   On the other hand, the quantitative oxidation of thionalid by iodine can be applied in the titrimetric determination of certain metals.   The stable, insoluble metal thionalid is isolated, decomposed with acid, and the liberated reagent is then titrated.   Colorimetric determinations can be based on the reduction by thionalid of phosphomolybdic acid, colloidal molybdenum blue being formed.

The Cobalt and Nickel Salts of Thioglycolic Acid Anilide

Thioglycolic acid anilide, C_6H_5—NH—CO—CH_2—SH, was briefly mentioned on p. 232 because its precipitating action is analogous to that of thionalid.   However, it merits some special discussion because of: (1) its behavior toward ammoniacal cobalt solutions; and (2) the composition and properties of its cobalt and nickel derivatives.   These compounds give interesting insights into the constitution of the inner complex salts of thioglycolic acid anilide and also of those derived from the homologous thionalid.   Bersin[88] found that a red-brown precipitate, which gradually turns brown, is produced by adding an alcohol solution of thioglycolic anilide to an ammoniacal solution of cobalt salts.   The precipitate is completely insoluble in 2 N hydrochloric acid, a fact that is utilized in the detection of cobalt.   This test, which is strictly specific in the presence of metal ions of the ammonium sulfide group, has a precipitation sensitivity of 1:10,000,000.   By varying the conditions, Bersin succeeded in isolating two distinct cobalt compounds.   If the precipitation is carried out at room temperature and the product is filtered off at once, a red-brown salt is obtained.   Higher temperatures and more prolonged action of the reagent yield a brown salt. • The Co:S ratio in the red-brown salt is 1:3, in the brown salt 2:3.   Bersin proved definitely that

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[87] A search for suitable stabilizers would be appreciated.   According to TH. BERSIN [Z. anal. Chem. **85**, 428 (1931)], 0.1% of alcoholic 8-hydroxyquinoline stabilizes thioglycolic acid anilide.   Accordingly, a similar effect can be expected with thionalid Ascorbic acid may possibly serve as stabilizer.

[88] TH. BERSIN, Z. anal. Chem. **85**, 428 (1931).

both compounds contain trivalent cobalt, formed by autoxidation.[89] The analytical figures indicate that the red-brown product is an inner complex salt, with the constitution (Ia) or (Ib). The brown salt quite probably can be represented by (II). The transformation of the red-brown salt into the brown salt argues in favor of (Ib).

$$C_6H_5-\overset{H}{\underset{|}{N}}-C=O$$
$$\underset{H_2C-S}{\overset{|}{}}\diagup Co/3$$
(Ia)

$$C_6H_5-N=\overset{H}{\underset{|}{C}}-O$$
$$\underset{H_2C-S}{\overset{|}{}}\diagup Co/3$$
(Ib)

$$\left[C_6H_5-N=\underset{\underset{H_2C-S}{|}}{C}-O\diagdown Co/3\right] Co/3$$
(II)
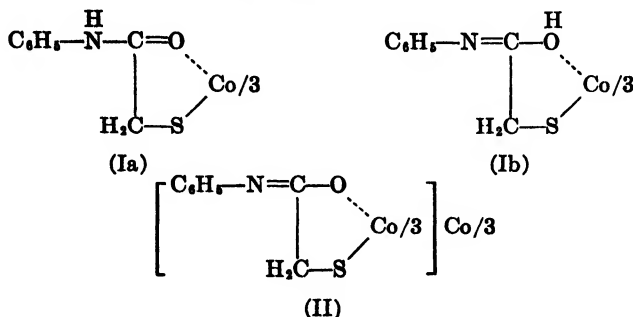
The coordination formula (II), in which one-half of the cobalt is a constituent of the inner complex anion, and the other half appears as a non-complex cation, shows that thioglycolic anilide can function as a dibasic acid. This is made possible by the enolization of the CO group.[90]

[89] It is rather remarkable that a cobaltic compound forms in the solution of a mercapto compound, which not only is a strong reducing agent, but also is itself readily subject to autoxidation. This provides a nice illustration of the fact that trivalence of the metal is favored in inner complex cobalt compounds. A study by L. MICHAELIS and S. YAMAGUCHI [*J. Biol. Chem.* **83**, 367 (1929)] should be consulted in this connection. They found that cobaltous salts on treatment with buffered solutions of cysteine undergo autoxidation and form the stable, brown inner complex anion.

$$\left[Co\left(\underset{\underset{H_2}{\overset{|}{N}}-\underset{}{\overset{|}{C}}-COO}{\overset{S-CH_2}{\overset{|}{}}}\right)_3\right]^{---}$$
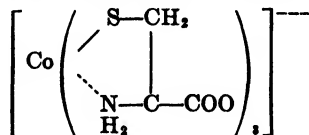
This case likewise involves an inner complex cobalti salt of a mercapto compound. These workers state that its formation can be used as the basis of a micro colorimetric method of determining cobalt or cysteine.

[90] The author agrees with Bersin (*loc. cit.*) in the assumption that the enolization is brought about by the migration of an atom of hydrogen from the NH group. This could be experimentally verified by a study of the behavior of the N-methylated thioglycolic anilide $C_6H_5-N(CH_3)-CO-CH_2-SH$. The latter could only form cobalt salts of type (I), if the enolization proceeds from the NH group. Should it be found, however, that the methylated derivative also produces cobalt salts of type (II), then it would be necessary to assume that the enolization involves an atom of hydrogen of the adjacent CH$_2$ group.

Consequently, it is necessary to assume a reactivity in either of the tautomeric forms:

$$C_6H_5{-}\underset{\underset{H}{|}}{N}{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{SH}{|}}{CH_2} \rightleftharpoons C_6H_5{-}N{=}\underset{\underset{OH}{|}}{C}{-}\underset{\underset{SH}{|}}{CH_2}$$
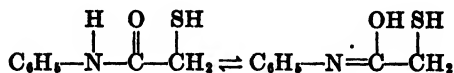
which are mono- and dibasic, respectively. Bersin isolated the brown nickel salt of thioglycolic anilide and its behavior corroborates the foregoing conclusions. The nickel salt dissolves in caustic alkali to form a light violet solution. This behavior points to the following coordination formula and reaction of a compound with an enolic OH group:
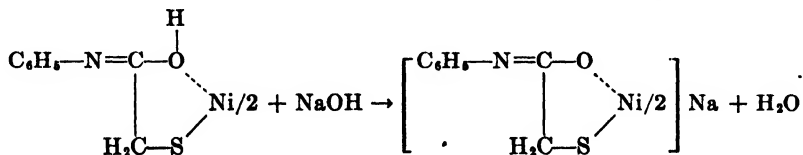
Accordingly, the soluble sodium salt of a dibasic acid with an inner complex nickel-bearing anion is formed from an insoluble inner complex nickel salt of the monobasic thioglycolic acid anilide.[91]

The author has found that the action of thionalid toward cobalt and nickel salts is entirely like that observed by Bersin with thioglycolic anilide. Consequently, the possibility of reaction in tautomeric forms must be taken into account in the case of thionalid also, and the possible presence of unsalified coordinately-bound enolic OH groups in its inner complex salts cannot be ruled out. Three different structures were accordingly presented (see p. 230) for the coordination formulas of the inner complex salts of thionalid. Which of these applies to the various inner complex salts cannot be stated with certainty. However, the solubility rule given on p. 409 affords some guidance. It states that inner complex salts, whose molecules still contain free acidic or basic groups, are only slightly soluble or insoluble in chloroform. Table IV (p. 231) shows that some metal thionalids dissolve well in chloroform, while others are not more than slightly soluble or practically insoluble. It can thus be assumed that the chloroform-insoluble metal thionalids

[91] Experimental support can be cited for the author's interpretation of Bersin's discovery that this nickel salt is soluble in alkali. It has been found that its solution in alkali produces a red precipitate with ferrous dipyridyl sulfate. The latter compound is a characteristic precipitant for complex anions (see p. 322). It may also be noted that information about the constitution of the insoluble, inner complex nickel salt could be derived by investigating the behavior of N-methylated thioglycolic anilide. If the enolization proceeds from the NH group, the N-methylated compound would produce a nickel salt that is not soluble in alkali (compare the preceding footnote).

have the same structure with respect to inner complex rings as the cobalt and nickel glycolic anilides just discussed. These latter salts, which, as has been shown, indubitably contain enolic OH groups, actually show no or very slight solubility in chloroform, thus conforming to the solubility rule.

Selective Precipitations with Mercaptobenzothiazole

Spacu and Kuraš[91a] showed that mercaptobenzothiazole (I) has selective precipitating action. This compound dissolves well in the ordinary organic solvents, and, since it is a mercaptan with pronounced acidic characteristics, it is also quite soluble in ammonia and alkali hydroxides and carbonates. Its solution in alcohol or acetone forms precipitates on treatment with acidified, hydrolysis-acid, or neutral solutions of Au, Ag, Cu, Pb, and Bi salts. Ammoniacal solutions of mercaptobenzothiazole react in the same way and, in addition, give precipitates with neutral or ammoniacal solutions of Ag and Tl salts. Among the precipitates studied by Spacu and Kuraš, only the copper and bismuth compounds have a decided color. The respective appearance of the products is given in the following tabulation:

Au.....	white	Bi. .	chrome yellow
Ag......	white	Pb . . .	light yellow or white
Hg..	white	Cd.	white
Cu..... . ..	orange-yellow	Tl..............	whitish yellow

The precipitates thrown down from neutral or slightly acid solution are salts of mercaptobenzothiazole (I), which contain one equivalent of metal for each mercaptobenzothiazole radical. This is shown in (II), which is the general formula for salts of divalent metals:
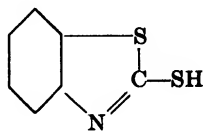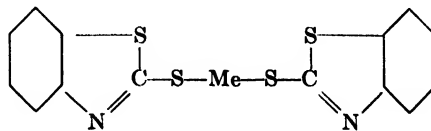
(I)   (II)

When Bi^{+++} and Pb^{++} ions react with mercaptobenzothiazole, there is a strong tendency to form basic salts. This is shown by the fact that the precipitates are not formula-pure, but come down with varying amounts of basic salt. A normal lead precipitate that contains only a little admixed basic salt is bright yellow; on digestion with warm, con-

91a G. Spacu and M. Kuraš, Z. anal. Chem. 102, 24, 108 (1936).

centrated ammonia this product is transformed quantitatively into the formula-pure, white basic salt (III). The white cadmium salt can be precipitated, from ammoniacal solution, as a diammine with the structure (IV). The added ammonia molecules are lost if the salt is heated to 110 to 120°C.

(III)   (IV)
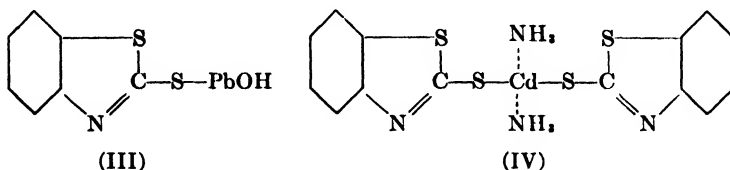
Members of the arsenic and molybdenum groups are not among the metals precipitable by mercaptobenzothiazole. This nonreactivity is rather remarkable, as these metal acid-forming elements have a pronounced affinity for sulfur, which is evidenced by the existence of stable sulfides of As, Sb, Mo, W, and V. Apart from these, it is precisely those metal ions which precipitate as sulfides from acid solutions saturated with hydrogen sulfide, which react with mercaptobenzothiazole to form precipitates. Consequently, there is here a distinct and sharply marked divergence from the precipitating action of SH^- ions, even though the ions of mercaptobenzothiazole can be regarded as organic derivatives of these inorganic ions. A notable exception is the Tl^+ ion; its sulfide can be precipitated only from alkaline but not from acid solution. Nevertheless, it is the only ion of the $(NH_4)_2S$ group that is quantitatively precipitable by mercaptobenzothiazole. It thus appears as though thallium has an especially great tendency to form insoluble monomercapto salts. It was pointed out on p. 232, in the discussion of thionalid, that the precipitation of thallium occurs under conditions at which all other thionalid precipitations fail.[91b]

Since, with the exception of the bismuth salt, the other insoluble salts of mercaptobenzothiazole are white or light yellow, Spacu and Kuraš considered the orange-yellow color of the copper salt, its resistance to ammonia, and its inability to form an ammine analogous to that of the cadmium salt, as evidence of its being an inner complex salt. They gave serious consideration to the coordination formulas (V) and (VI), and these have been accepted in all the monographs on organic reagents.

[91b] It would be interesting to learn whether other mercaptans also show a marked Tl affinity. As a check or for comparison purposes, the mercaptans studied by J. Dubsky and his associates [Z. anal. Chem. 98, 184 (1934)] with respect to their behavior toward Bi^{+++} ions, could be used.

(V)   (VI)
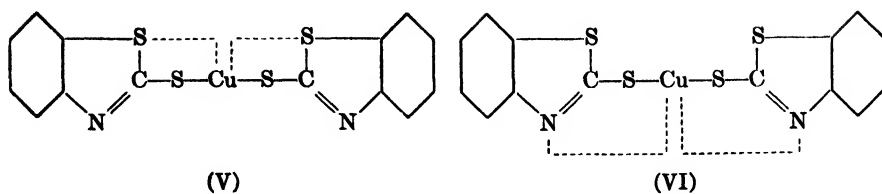
However, objections can be offered against these structures. All experience shows that inner complex salts contain 5- or 6-membered rings, formed through principal and auxiliary binding of metal atoms. The proposed formulas require the assumption of 4-membered rings. Furthermore, the copper salt does not exhibit the solubility in organic liquids that is so often shown by inner complex salts, nor does it exhibit any striking difference from the other insoluble salts of mercaptobenzothiazole, which are regarded as normal salts by these workers. Hence, the only remaining noteworthy reason for the assumption that the copper salt is an inner complex salt is its inability to coordinate ammonia molecules. However, even this reason is not valid because studies (unpublished) by the writer show that the copper precipitate is not a cupric salt of mercaptobenzothiazole, of the composition $Cu(SR)_2$. It actually is a cuprous salt mixed with the equivalent quantity of the water-insoluble disulfide of the mercaptan, and has the composition $Cu_2(SR)_2 + (R—S—S—R)$. An analysis of the precipitate obviously can not reveal this fundamental difference because the percentage of copper is the same in both cases. Furthermore, it was found that considerable amounts of disulfide can be extracted by ether from a precipitate produced by the action of excess copper solution. In addition, it was established that cuprous salts (*e.g.*, copper sulfate solution decolorized by sulfite), on treatment with mercaptobenzothiazole, immediately form an orange-yellow precipitate that cannot be distinguished externally from the precipitate produced by the action of cupric salts. This behavior corresponds completely to that shown by cupric and cuprous salts toward alkali thiocyanate and alkali xanthate in acid solution. With these compounds also, which are closely allied to mercaptobenzothiazole by their SH group content, cuprous salts produce an immediate precipitate of white cuprous thiocyanate or yellow cuprous xanthate, whereas cupric salts produce an initial precipitate of the black cupric compounds, which rapidly transform to the corresponding cuprous compounds, with accompanying change of color and simultaneous production of disulfide. An intermediate formation of cupric mercaptobenzothiazole also occurs when cupric ions are added to alcohol solutions of mercaptobenzothiazole. Spacu and Kuraš pointed out that under

these circumstances a blue-green precipitate appears at first in the cold, and this, on heating, changes rapidly into the orange-yellow product. However, they erroneously thought the initial precipitate was a basic salt, even though it seems more likely, because of more intensive hydrolysis, that a basic salt would be formed on heating. The reaction of cupric ions with mercaptobenzothiazole, accordingly, can be represented as a redox reaction:

$$2R\text{---}S^- + 2Cu^{++} \rightarrow 2Cu^+ + R\text{---}S\text{---}S\text{---}R$$
$$2R\text{---}S^- + 2Cu^+ \rightarrow R\text{---}S\text{---}Cu\text{---}Cu\text{---}S\text{---}R$$
$$(R\text{---}S^- = \text{anion of mercaptobenzothiazole})$$
$$(R\text{---}S\text{---}S\text{---}R = \text{disulfide of mercaptobenzothiazole})$$
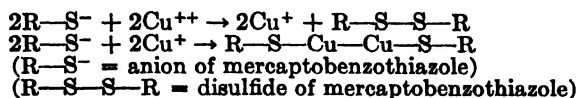
In all likelihood, according to unpublished studies by the author, the precipitate formed by the action of auric salts with mercaptobenzothiazole, and which Spacu and Kuraš thought to be $Au(SR)_3$, is likewise the result of a redox reaction, which leads to the production of aurous mercaptobenzothiazole and the corresponding disulfide. As in the case of the copper precipitate, analysis of the gold product tells nothing as to whether $Au(SR)_3$ or $Au(SR) + (R\text{---}S\text{---}S\text{---}R)$ is being studied, since both products contain the same percentages of metal, sulfur, and nitrogen.

Spacu and Kuraš report that the precipitation of copper, cadmium, lead, *etc.*, can serve for the quantitative determination of these metals and for their separation from others which do not react with mercaptobenzothiazole. A convenient method of separating copper and cadmium is based on the precipitability of copper by this reagent and the non-precipitability of cadmium from weakly acidified solution. The precipitates produced by the use of alcohol or acetone solutions of the reagent are not formula-pure because they are contaminated with the disulfides, which are always present in these solutions and which precipitate on dilution with water. Such precipitates must be ignited to the corresponding oxide, or to the metal in the case of gold. The examples of the precipitation of the lead, cadmium, and thallium salts show that freshly prepared ammoniacal solutions of the reagent seem to yield formula-pure precipitates that are free of disulfides and suitable for use as weighing forms. It may be expected that the silver precipitate, produced from ammoniacal solution, and also the precipitates formed from masked ammoniacal solutions of metal salts, will be of interest with respect to new gravimetric procedures. In passing, it should be pointed out that bismuth, in contrast to lead, is not precipitable by mercaptobenzothiazole from tartrated ammoniacal solutions.

An interesting behavior of mercaptobenzothiazole was observed in studies on new inner complex salts of trivalent thallium.[91c] Solutions of

[91c] F. FEIGL, *Nature* **161**, 436 (1948).

Tl^{III} salts, which were masked against hydroxide precipitation by tartaric or sulfosalicylic acid, give a chrome yellow precipitate with ammoniacal solutions of mercaptobenzothiazole. Within a few minutes, this product assumes the whitish yellow color of the thallous mercaptobenzothiazole. The transient formation of a yellow precipitate can be seen in acid thallic solutions also. Obviously, this case is fully analogous to that of the copper precipitate, and probably of the gold precipitate; there is a primary precipitation of yellow thallic mercaptobenzothiazole, and this then decomposes into white thallous mercaptobenzothiazole and the disulfide of mercaptobenzothiazole. It is interesting to note that thionalid, which was discussed on p. 231, and which gives an orange-yellow thallous salt, forms a white precipitate of thallic thionalid with either acid or masked ammoniacal thallic solutions. Accordingly, of these two mercaptans, the thallic compound of thionalid is stable but not that of mercaptobenzothiazole. This difference is plausibly explained by a scrutiny of the respective formulas of these products. Only the thionalid compound is an inner complex salt, whereas the mercapto-benzothiazole compound is a normal salt:
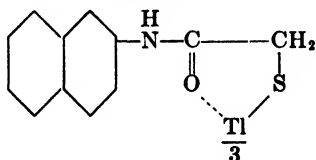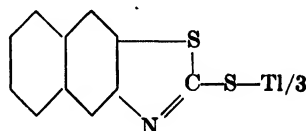
Stable inner complex salt   Unstable normal salt

It has been found repeatedly that complex compounds often contain metals with valences which either do not occur in normal salts, i.e., in compounds possessing principal valences only, or such valences are not stable. The possibility of a stabilization through inner complex binding is, therefore, clearly the reason why stable cupric and auric compounds are formed by thionalid and not by mercaptobenzothiazole. Because of the inner complex binding, which leads to extremely insoluble salts, the usual characteristic redox reaction by which SH groups form disulfide does not take place in the case of thionalid, but proceeds as usual with mercaptobenzothiazole. Consequently, the cupric, auric, and thallic salts of thionalid present the interesting case that, in these inner complex salts, both of the reactants are stabilized. The behavior of thionalid and mercaptobenzothiazole toward Cu^{II}, Au^{III}, and Tl^{III} salts have been contrasted here because the stability of the salts of thionalid and the instability of the mercaptobenzothiazole salts offer a nice proof that mercaptobenzothiazole is not an inner complex-forming reagent. The fundamentally important problem of complex chemistry, namely, whether

inner complex salts possessing four-membered rings are possible, has by no means been answered positively by the behavior of mercaptobenzothiazole. The response seems rather to be negative.

The remarkable behavior of platinum and palladium salts toward mercaptobenzothiazole has not been studied before. These noble metals form precipitates that are bright yellow or brown-red, respectively. The precipitation with palladium is especially sensitive. The action of platinum and palladium salts is in agreement with the fact that these noble metal ions are precipitable as sulfides by hydrogen sulfide from acid solutions, and hence, in this respect, they behave like the other metals which are precipitable by mercaptobenzothiazole. Palladium can also be thrown down from an ammoniacal solution. This finding deserves particular notice because neither dimethylglyoxime nor 1-nitroso-2-naphthol produces a precipitate with ammoniacal palladium solutions. The inner complex salts of these organic reagents with palladium are formed only from neutral or mineral acid solutions. The precipitation of these inner complex salts is masked in ammoniacal solution, where the metal is present as stable $[Pd(NH_3)_2]^{++}$ ions. Consequently, since mercaptobenzothiazole precipitates palladium from ammoniacal solutions, the solubility product of this normal salt must be smaller than that of the inner complex salt of palladium with dimethylglyoxime or 1-nitroso-2-naphthol. It can be predicted that mercaptobenzothiazole will serve for the gravimetric determination of palladium.

The Analytical Behavior of Diphenylthiocarbazone (Dithizone)

Cazeneuve[92] discovered that diphenylcarbazide (I) reacts with mercury and other heavy metal salts to produce colored (usually blue to blue-violet) precipitates. He also observed that chromates, in strong acid solution, give an intense red-violet color with this reagent. These reactions can be used as sensitive methods of detection, and they were among the first tests employing organic reagents that proved to be especially adapted to spot test analyses.[93] The chromate reaction of diphenylcarbazide has become particularly important, because it is strictly specific if the sample contains no vanadium. It is widely used in the colorimetric determination of small amounts of chromium.[94] Although the chemistry of the chromate reaction has not been cleared

[92] P. Cazeneuve, Compt. rend. 131, 346 (1900); Bull. soc. chim. 23, 701 (1900); 25, 761 (1901).

[93] Compare F. Feigl, Spot Tests, pp. 49, 128, etc.

[94] This procedure was first described by A. Moulin, Bull. soc. chim. 31, 295 (1904); compare G. P. Rowland, Ind. Eng. Chem., Anal. Ed. 11, 442 (1939).

up,[95] Feigl and Lederer[96] proved that colored inner complex heavy metal salts of the type (III) or (IIIa) are formed when diphenylcarbazide reacts with metal ions.   Diphenylcarbazide is oxidized by the air to diphenylcarbazone (II), and it should be noted that both of these compounds can function as salt-formers.   The terminal NH group is assumed to be the salt-forming group:
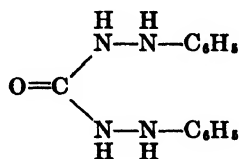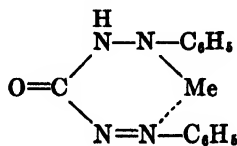
$$(I) \qquad (II)$$
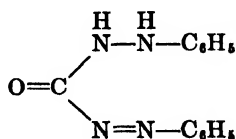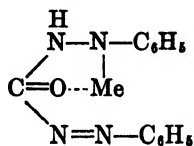
$$(III) \qquad (IIIa)$$

Fischer[97] had the happy inspiration to test the analytical behavior of the sulfur analogue of diphenylcarbazone, namely, diphenylthiocarbazone.   As was expected, it not only proved capable of forming inner complex salts but it also displayed advantageous properties that are superior to those of its oxygen analogue.   There is an analogy here to the comparative behavior of rubeanic acid (see p. 248) and the dithiols (see p. 226) with their oxygen homologues.   The activity of the sulfur atom is manifested by an intensification of the color of the salts, and also in the marked enolizing ability of the $>$C$=$S group.   The deep color of the inner complex metal compounds and their excellent solubility in many organic liquids have made it possible to develop a large number of tests for heavy metals and, more particularly, methods of quantitatively determining them.   Some of these involve entirely new procedures.   Fischer's numerous studies[98] have been almost entirely responsible for

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[95] The author believes that a heteropolyacid may be formed between chromic acid and diphenylcarbazide (diphenylcarbazone).   Experimental proof is lacking, because the pure products have not yet been isolated.

[96] F. FEIGL and H. LEDERER, *Monatsh.* **45**, 63, 115 (1924).

[97] H. FISCHER, *Wiss. Veröffentl. Siemens-Konzern* **4**, 158 (1925).

[98] The many papers by H. FISCHER and his collaborators have appeared in the *Zeitschrift für analytische Chemie* and the *Zeitschrift für angewandte Chemie* since 1925.

the elucidation of the fundamental reactions, as well as the development of the procedures themselves.   He named the reagent "dithizone."

Dithizone is a violet-black solid, which is difficultly soluble in most organic liquids.   The best solvents are chloroform and carbon tetrachloride.   The intense green color of these solutions often gives a false impression of the solubility, which actually is quite low.   For instance, about 20 mg. of dithizone will saturate 100 ml. of carbon tetrachloride. These two solvents are the only ones that are used in preparing dithizone solutions for analytical purposes.   When the reagent solution is shaken with an aqueous solution of a reacting metal, the resulting inner complex salt nearly always dissolves in the organic layer, to which it imparts a violet, red-orange, or yellow color, depending on the metal involved. This procedure of forming a salt and immediately extracting it is practiced in all analytical applications of dithizone.

<div align="center">

TABLE V

Metals Reacting with Dithizone
(The enclosed elements yield dithizonates)

</div>

H															
Li	Be										B	C	N	O	F
Na	Mg										Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Ti	Pb	Bi	Po	—
—	Ra	Ac	Th	Pa	U										

Dithizone is the only known acidic organic reagent, which, under the conditions of its practical analytical application, can function toward a given metal as either a mono- or a dibasic acid.   The monobasic action corresponds to a thioketoimid form of the reagent (I) (usually referred to as its keto form).   A terminal NH group is the salt-former in this case, as in the analogous diphenylcarbazone.   The dibasic action is due to a thioenolimid form (II) (enol form).   In this case, the acidic action of the NH group is supplemented by the action of an acidic SH group, produced by the enolization of the CS group contained in the keto form.[99]

$$S{=}C\diagup\diagdown\begin{array}{c}\overset{H}{\overset{|}{N}}{-}\overset{H}{\overset{|}{N}}C_6H_5\\[4pt]N{=}NC_6H_5\end{array}\qquad\qquad C\diagup\diagdown\begin{array}{c}\overset{H}{\overset{|}{N}}{-}\overset{H}{\overset{|}{N}}C_6H_5\\[4pt]SH\\[4pt]N{=}NC_6H_5\end{array}$$

<div align="center">(I)   (II)</div>
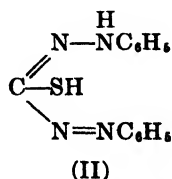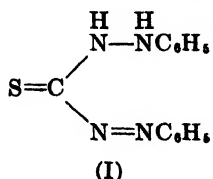
[99] Dithizone here reveals its descent from thiourea, which likewise can react in its thioenol form, as, for instance, in the oxidation by iodine to produce imine disulfide.

TABLE VI

The Dithizonates[a]

K = keto E = enol S = soluble I = insoluble

Metal	Com-plex	Color (CCl₄)	Solubility in CCl₄ or CHCl₃	pH for extraction	Remarks
Bismuth.......	K	Orange-yellow	S	>2 (CCl₄)	
	E	Orange-red	S	Basic soln.	See Reith and van Dijk, *Chem., Weekblad* **36**, 343 (1939). Also reacts in presence of KCN (pH 7–8).
Cadmium......	K	Red	S	Basic soln.	Stable when shaken with 1 N NaOH.
Cobalt........	K	Violet	S	7–9 (optimum in CCl₄)	Organic soln. of dithisonate quite stable to dilute mineral acids.
	E?	Brownish	S	Strongly basic soln.	May be decomposition product.
Copper (I).....	K	Violet	S	Dil. mineral acid soln. (ca. 0.1 N)	
(I)..........	E	Red-brown	S	Basic soln.	Only slightly soluble in CCl₄.
(II)........	K	Violet-red	S	Dil. mineral acid soln.	
(II)........	E	Yellow-brown	S	Basic soln.	Can also be formed in slightly acid soln. when copper is in excess of Dz.
Gold..........	..	Yellow	S (CHCl₃)	Dil. mineral acid soln.	Red color first appears on shaking; this quickly changes to orange and then to yellow. Flocs in CCl₄. Au (III) probably reduced to Au (I).
Indium........	..	Red	S	5–6 (CCl₄)	pH adjustment critical. Also reacts in presence of cyanide at pH 5–6.
Iron (II)......	..	Violet-red	S	6–7 (CCl₄)	Fe (III) does not form a complex but oxidizes Dz in basic medium, especially in presence of cyanide.
Lead..........	K	Cinnabar red	S	8.5–11 (optimum in CHCl₃)	
Manganese....	..	Violet-brown (CHCl₃)	S (CHCl₃)	ca. 11	Solution very unstable. Brown flocs in CCl₄.
Mercury (I)...	K	Orange	S	Dil. mineral acid soln.	
(I)..........	E	Purplish red	S	Basic medium	
(II)........	K	Orange-yellow	S	Dil. mineral acid soln.	Can also be formed in weakly alkaline solution with an excess of Dz.
(II)........	E	Purplish red	S	Basic medium	Can also be formed in slightly acid solution with a deficiency of Dz.
Nickel........	..	Brownish	S	Weakly basic medium	CCl₄ solution not easily decomposed by dilute mineral acids. From a strongly basic solution, CCl₄ extract is gray.

TABLE VI (*Continued*)

Metal	Complex	Color (CCl₄)	Solubility in CCl₄ or CHCl₃	pH for extraction *	Remarks
Palladium.....	E?	Brown-red (CHCl₃)	S(CHCl₃)	Dil. mineral acid soln.	Partly soluble in CCl₄ (dark violet). Reaction is slow.
	K	Brownish-green (CHCl₃)	S(CHCl₃)	....	By addition of Dz to solution of enol compound. Stable towards 6 N NaOH and 6 N H₂SO₄.
Platinum (II)..	..	Violet or violet-red aqueous layer; green CCl₄	....	Weakly acid solution	Probably a colloidal solution; sometimes violet flocs are obtained (insoluble in CHCl₃). Pt (IV) does not react; neither do other Pt metals in quadrivalent or trivalent state.
Silver........	K	Yellow	S	Dil. mineral acid soln.	
	E	Red-violet	I	Basic soln.	Slightly soluble in CHCl₃ (red solution).
Thallium (I)...	K?	Red	S	9–12 (CCl₄)	Also formed in presence of cyanide.
(III)........	K?	Yellowish red	S	3–4 (CCl₄)	Reaction not complete. Tl (III) also oxidizes Dz.
Tin (II).......	K	Red	S	> 4 (optimum 6–9 in CCl₄)	Not stable.
Zinc.........	K	Purplish red	S	Neutral or weakly basic soln.	With an excess of Dz extraction can be made complete in weakly acid medium.

ª Based on data of H. FISCHER and others, and upon SANDELL's observations.

The following coordination formulas and abbreviated symbols (DzH₂, DzH) apply to the inner complex salts of the tautomeric forms of dithizone with divalent metals:[100]
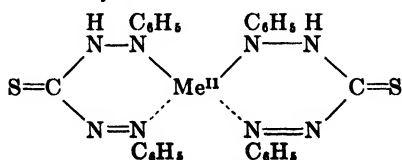
Thioketoimid form (keto form)   Thioenolimid form (enol form)
Me^{II}(DzH)₂   Me^{II}Dz

Fischer states that the keto form is the preferred salt form. It exists in the cases of all metals that are at all capable of forming dithizonates which are insoluble in water and soluble in organic liquids. On the other

[100] Fischer has designated the keto- and enol salts of dithizone as tautomers. Other workers followed this lead in their discussions of metal dithizonates. However,

hand, the enol form, whose color always differs from that of the keto form, is not encountered in all metal salts (see Table VI). The keto form, except in the case of the silver compound, can be transformed more or less readily into the enol form (if this exists) by the action of alkalies [Eq. (1)]. On the other hand, the enol form is changed to the keto form on treatment with acids [Eq. (2)]. If excess dithizone is present, reaction (3) follows (2).

$$Me(DzH)_2 + 2OH^- \rightarrow MeDz + Dz^{--} + 2H_2O \qquad (1)$$
$$2MeDz + 2H^+ \rightarrow Me(DzH)_2 + Me^{++} \qquad (2)$$
$$Me^{++} + 2DzH_2 \rightarrow Me(DzH)_2 + 2H^+ \qquad (3)$$
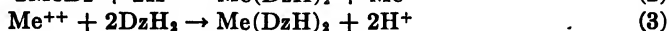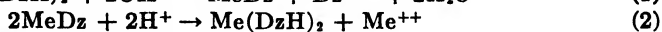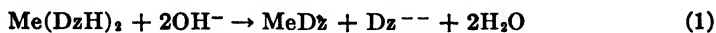
In accordance with the preceding equations, the keto forms are stable in acid or neutral solution. The enol forms are stable in weak alkaline solution. The ion Dz^{--} is shown in (1), which signifies that dithizone dissolves in alkali to form an alkali dithizonate. Basic aqueous solutions of dithizone are yellow.

Table V[101] shows the metals that form inner complex salts with dithizone.

It may be pointed out, with respect to Table V, that no metal dithizonate can be formed in strong acid solution. Furthermore, certain multivalent metals react only at one valence. For instance, Fe^{II}, Sn^{II}, and Pt^{II} react, but not Fe^{III}, Sn^{IV}, or Pt^{IV}. The reason probably is that reducible metal ions oxidize dithizone (by attack on the SH group) and then react in their reduced form with the excess dithizone. This is shown in Table VI, which summarizes the properties of a number of metal dithizonates.

Tables V and VI show that dithizone reacts with a considerable number of metal ions, and hence has very little specificity. However, variation of the reaction conditions can lead to an increased selectivity in the action of even this reagent. The most important of such modifications are adjustment of the pH of the solution to be extracted, and addition of masking agents that form complexes with the interfering metal ions.

When the total content of reacting metals is low, it is sometimes better not to extract a given metal from a solution of adjusted pH. It is

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this is open to question. The salts themselves are not tautomeric with each other, but only the two salt-producing forms of dithizone are thus related. As shown by the formulas $Me(DzH)_2$ and $MeDz$, these salts have an entirely different percentage composition. Tautomerism, by definition, requires identical percentage composition with differing modes of reaction. This is true only for the two forms of dithizone and not for its enol and keto salts.

[101] Tables V, VI and VII are reproduced from E. B. SANDELL's Colorimetric Determination of Traces of Metals, Interscience, New York, 1944.

preferable in these cases to extract under such conditions (for instance, from a faintly ammoniacal solution) that other metals are also extracted, and then to shake the separated organic layer containing the dithizonates with a dilute acid of appropriate concentration, so that only the desired metal either remains in the organic solvent or passes alone into the aqueous layer, while the other dithizonates remain undecomposed. For instance, if a carbon tetrachloride solution containing the dithizonates of copper, zinc, and lead is shaken with one or two portions of dilute acid (0.05 N or even weaker) the copper stays in the carbon tetrachloride, while the zinc and lead pass into the water phase.

Reagents that form stable complex salts with interfering metal ions play an important role in dithizone procedures. Table VII shows that the number of metals reacting with this reagent is greatly reduced in the presence of complex-forming reagents.

TABLE VII
Complex-Forming Agents in Dithizone Reactions

Conditions	Metals reacting
Basic solution containing cyanide.....	Pb, Sn^{II}, Tl^{I}, Bi
Slightly acid solution containing cyanide... ...	Pd, Hg, Ag, Cu
Dilute acid solution containing thiocyanate......... .	Hg, Au, Cu
Dilute acid solution containing thiocyanate + cyanide	Hg, Cu
Dilute acid solution containing bromide or iodide..........	Pd, Au, Cu
Slightly acid solution (pH 5) containing thiosulfate (CCl_4 solution of dithizone)........................	Pd, Sn^{II}, Zn (Cd)
Slightly acid solution (pH 4–5) containing thiosulfate + cyanide...........	Sn^{II}, Zn
Citrate and tartrate in basic medium....	Usually do not interfere with extraction of reacting metals

Dithizone procedures are less important in qualitative inorganic analysis than in quantitative work. This reagent is particularly useful in trace analysis, where colorimetric procedures based on its action can be applied to solve problems which formerly were either impossible, or required roundabout tedious methods.[102] The solubility of metal dithizonates in chloroform and carbon tetrachloride is the chief factor that makes it feasible to extract these salts from large volumes of liquid, and to bring them into workable concentrations from dilutions where they constituted no more than traces. After the metal dithizonates have thus been collected in a small volume of chloroform or carbon tetrachloride, the solvent can be volatilized, and the residue subjected to

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[102] E. B. SANDELL, *op. cit.* discusses this topic and gives technical details of the procedures.

identification tests and quantitative procedures. Heller[103] has given a nice example of this in his method of identifying and determining traces of heavy metals in water.

Suprunovich[104] has shown that di-β-naphthylthiocarbazone has, in general, the same properties as dithizone. However, the colors of the inner complex heavy metal salts are deeper, and hence the sensitivity of the identification tests is higher if this naphthyl analogue is used in place of dithizone. The deepened color resulting from this substitution of the phenyl group by the naphthyl group is shown in the following comparison:

	Color in Chloroform	
Metal	*Dithizone*	*Naphthyldithizone*
Mercury	Yellow-orange	Red (bluish shade)
Lead	Rose-red	Purple
Bismuth	Orange	Magenta

Hubbard and his collaborators[105] accordingly used dinaphthylthiocarbazone for the colorimetric determination of small amounts of mercury and zinc in biological specimens. They prepared several other homologues of dithizone, but none of these exhibited any special advantages.[105a]

The Selective Activity of Rubeanic Acid

Rubeanic acid is dithiooxamide (I), *i.e.*, it is the sulfur analogue of oxamide (II):

$$S=C-NH_2 \qquad\qquad O=C-NH_2$$
$$S=C-NH_2 \qquad\qquad O=C-NH_2$$
$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$
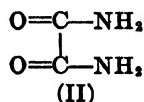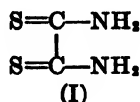
The replacement of oxygen by sulfur generally brings about characteristic alterations in the properties of organic compounds; almost always the color is deepened, and the acidic character is increased. A comparison of oxamide and rubeanic acid bears out this statement. The former is colorless, only slightly soluble in organic liquids, and does not form salts with either acids or alkalies. In contrast, dithiooxamide is yellow-red, dissolves in organic liquids, and its acid character is evidenced by its ready solubility in alkali hydroxides (alkali salt formation). The acidic character of rubeanic acid is due to the tautomerism existing between its diamido (baso), amidoimido (semiaci), and its diimido (aci) forms:

[103] K. HELLER, G. KUHLA and F. MACHEK, *Mikrochemie* **18**, 193 (1935).

[104] J. B. SUPRUNOVICH, *Chem. Abstracts* **33**, 1306 (1939).

[105] D. M. HUBBARD, *Ind. Eng. Chem., Anal. Ed.* **12**, 768 (1940); J. CHOLAK, D. M. HUBBARD and R. E. BURKEY, *ibid.* **15**, 754 (1943).

[105a] Compare also R. E. OESPER and J. KLINGENBERG, *J. Org. Chem.* **18**, 309 (1948).

$$
\begin{array}{ccc}
\text{S}=\text{C}-\text{NH}_2 & \text{HS}-\text{C}=\text{NH} & \text{HS}-\text{C}=\text{NH} \\
| & \rightleftharpoons \quad | & \rightleftharpoons \quad | \\
\text{S}=\text{C}-\text{NH}_2 & \text{S}=\text{C}-\text{NH}_2 & \text{HS}-\text{C}=\text{NH} \\
\text{baso form} & \text{semiaci form} & \text{aci form}
\end{array}
$$
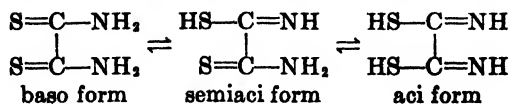
In water-alcohol solution, the following tautomerism and dissociation equilibria must be taken into account:

$$
\begin{array}{ccccc}
\text{S}=\text{C}-\text{NH}_2 & & \text{HS}-\text{C}=\text{NH} & & \left[\begin{array}{c} -\text{S}-\text{C}=\text{NH} \\ | \\ \text{S}=\text{C}-\text{NH}_2 \end{array}\right]^{-} \\
| & \rightleftharpoons & | & \rightleftharpoons & \quad + \text{H}^+ \\
\text{S}=\text{C}-\text{NH}_2 & & \text{S}=\text{C}-\text{NH}_2 & & \\
& & \updownarrow & & \\
& & \text{HS}-\text{C}=\text{NH} & & \left[\begin{array}{c} -\text{S}-\text{C}=\text{NH} \\ | \\ -\text{S}-\text{C}=\text{NH} \end{array}\right]^{--} \\
& & | & \rightleftharpoons & \quad + 2\text{H}^+ \\
& & \text{HS}-\text{C}=\text{NH} & &
\end{array}
$$
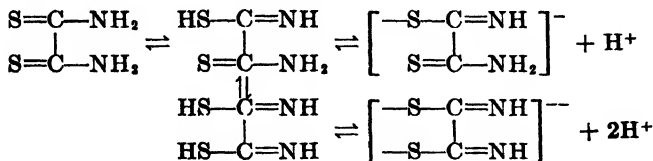
In accord with these equilibria, it is possible to increase the concentration of the rubeanate anions considerably by suppressing or removing H^+ ions (*e.g.*, by addition of alkali acetate or hydroxide). Conversely, the addition of H^+ ions will decrease the concentration of rubeanate anions. The selective action of rubeanic acid is determined by the position of the baso-aci equilibrium, and by the prevailing concentration of rubeanate anions.

Rây[106] was the first to show that copper, nickel, or cobalt can be precipitated quantitatively, from ammoniacal solution, as rubeanates. The copper salt is dark green, cobalt rubeanate is brown-red, and nickel rubeanate is violet. These compounds can be represented as inner complex salts.
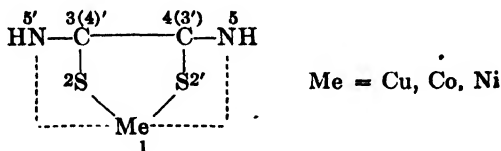
The numbering in the coordination formula shows that, through the action of principal and auxiliary valences of the metal atoms, it is possible to form two overlapping five-membered rings (1, 2, 3, 4, 5, and 1, 2', 3', 4', 5'). The intense color of the metal rubeanates is obviously due to these ring systems that are so characteristic of inner complex compounds. Accordingly, the tests with rubeanic acid, recommended by Rây, for copper, cobalt, and nickel are very sensitive. In fact, no other organic reagent for copper is as sensitive. It is noteworthy that only colored, ammine-forming heavy metal ions produce colored rubeanates. Rubeanic acid does not precipitate the corresponding salts from ammoniacal zinc and cadmium solutions. Instead, white zinc sulfide and yellow cadmium sulfide are deposited. Rây (*loc. cit.*) states that yellowish white Cd

[106] P. RÂY, *Z. anal. Chem.* **79**, 94 (1929).

rubeanate is produced initially and goes over into the yellow sulfide on warming.

The concentration of rubeanate anions necessary for the precipitation of Cu^{++}, Co^{++}, and Ni^{++} ions increases in this order. Accordingly, copper can be precipitated quantitatively, even from weak mineral acid solutions, whereas cobalt or nickel rubeanate comes down only if the mineral acid solution is buffered with acetate. None of these three rubeanates can be precipitated from solutions that contain considerable concentrations of free mineral acids. On the other hand, after these salts have been precipitated from ammoniacal solutions, they are quite resistant to mineral acids. This is shown especially well by the cobalt and nickel salts, which are quite stable toward even 1:1 dilute hydrochloric or sulfuric acid, at room temperature. Although Cu rubeanate can be precipitated from weak acid solution, it is less resistant to acids than the Ni and Co salts.

Wölbling and Steiger[107] showed that palladium, platinum, and gold can be precipitated from strong mineral acid solutions by rubeanic acid. The palladium precipitate is brown-red; the gold salt is yellow at first, and turns brown on heating. The reaction with platinum salts which leads to a brown-black precipitate proceeds very slowly, and possibly should be considered as forming PtS_2. The palladium salt, according to these workers, has the composition:

$$S=C-NH_2$$
$$|\qquad\diagdown$$
$$\qquad\quad Pd/2 + 1 \text{ Rubeanic acid}$$
$$HN=C-S\diagup$$
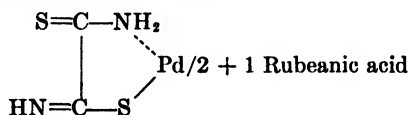
This corresponds, therefore, to a palladium salt of the semiaci form of dithiooxamide and its existence is evidence in support of the view that the production of a semiaci form (see preceding equilibria) should also be taken into account when considering these tautomerism and dissociation equilibria.[106a] The composition of the gold precipitate is not known. Rubeanic acid produces a blue color in glacial acetic acid solutions of ruthenium salts, an effect that can be used to detect small quantities of this element. The composition of the blue ruthenium product is not known.

Rubeanic acid precipitates zinc and cadmium as sulfides (see p. 249). Consequently, in addition to a direct formation of salts, as has been

[106a] The Pd compound is probably a salt of the semiaci form of dithiooxamide. However, the possibility of a Pd salt of the acid form coordinated with 2 molecules of rubeanic acid cannot be excluded. The precentage composition is the same in both cases.

[107] H. WÖLBLING and B. STEIGER, *Mikrochemie* **15**, 295 (1934).

proved with Cu, Co, Ni, and Pd, it is also necessary to consider a decomposition reaction, involving the removal of sulfur from the rubeanic acid. Actually, a decomposition of this kind is observed when this reagent reacts with Ag, Pb, and Hg salts; they produce the respective sulfides. Possibly, unstable rubeanates are the initial products of these reactions, and they are subsequently hydrolyzed with formation of sulfide and oxamide. The quite stable rubeanates of copper, cobalt, and nickel are decomposed on treatment with silver nitrate; Ag_2S results. This action is readily observed if a drop of silver nitrate solution is placed on filter paper impregnated with one of these rubeanates. A brown to light yellow fleck, depending on the quantity of silver, forms on the colored paper. H. Suter (unpublished study) found that 5γ silver can be revealed distinctly in this way.

When rubeanic acid reacts with Cu^{++}, Co^{++}, Ni^{++}, and Pd^{++} ions, the action is due to the groups:
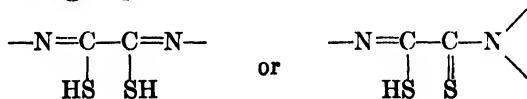
In line with this is the unpublished finding by Feigl that dimethyl-, diethyl-, and diphenyldithiooxamide show the same behavior toward these ions as the parent compound. No significant chromotropic effect is obtained by the introduction of the alkyl groups; nor are there any recorded differences in sensitivity. The behavior of alkyl derivatives of rubeanic acid toward the metals of the platinum group has not been studied. An intensive study of the analytical behavior of the mono- as well as of the symmetric and unsymmetric dialkylated dithiooxamides would be valuable in extending the available knowledge of the analytical actions of atomic groupings.

Acidic NOH Groups

Acidic NOH groups may be original components of organic compounds or they may be formed from NO or NO_2 groups by enolization of an oxygen atom. In the former case, the compound, as evidenced by the method by which it was prepared, is invariably a derivative of hydroxylamine. Although the latter *per se* is a base, its NOH group can be forced to take on an acidic character. This can be accomplished either by binding the nitrogen atom to two negative radicals (compare the arylnitrosohydroxylamines, p. 262) or by double-bonding it to a carbon atom,

as in $\diagdown C{=}NOH$, to form an oxime. When an NO group is converted into an NOH group through enolization, the requisite atom of hydrogen

shifts from an adjacent OH—, CH—, or CH$_2$— group. In such instances, an equilibrium is always set up between the NO and the NOH groups. This equilibrium is displaced in favor of the NOH form by OH⁻ ions, while H⁺ ions cause a shift toward the NO form. Such materials are called isonitroso compounds, a name that indicates their origin and also the fact that they never completely lose the character of an NO (nitroso) compound. It should be noted that the NOH group when it produces salts with heavy metals can function in its tautomeric form by virtue of a change in valence of the nitrogen. The metal is bound either:

$$=N—O—Me, \quad or \quad =\overset{\overset{O}{\|}}{N}—Me \quad \text{(oximine or amine oxide form)}.$$

When not salified, the two forms can be distinguished by their behavior toward alkali hydroxide solutions. Compounds with =N—OH groups are readily soluble in these basic solutions, whereas compounds containing

$$=\overset{\overset{O}{\|}}{N}—H$$

groups dissolve with difficulty or practically not at all. True isonitroso compounds have excellent alkali-solubility, and hence belong to the =N—OH form.

Enolization in alkaline solutions of an NO$_2$ group bound to carbon can produce an alkali salt of the acidic $=\overset{\overset{O}{\|}}{N}OH$ group. It appears as though this enolization and the dependent formation of heavy metal salts is of special analytical importance among aromatic nitro compounds.

A study of the organic reagents carrying NOH groups of the types noted in the following paragraphs makes it clear that selective actions occur almost exclusively when the salt formation, by replacement of the acidic hydrogen with a metal, is combined with an auxiliary valence involvement with adjacent atoms. Inner complex salts result. The tendency to form these complex salts is so marked that, for example, only one NOH group is salified in 1,2-dioximes, while the other NOH group merely coordinates through its nitrogen atom.

Selective Actions of Nitrosonaphthols

If organic reagents that form colored precipitates with metal ions were arranged in the chronological order of their discovery, the list would be headed by 1-nitroso-2-naphthol. This compound was prepared in 1884 by Ilinski.[108] Almost immediately it was found to be a precipitant

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[108] M. ILINSKI and G. v. KNORRE, *Ber.* **18**, 699, 2728 (1885); G. v. KNORRE, *ibid.* **20**, 283 (1887); *Z. angew. Chem.* **6**, 264 (1893); **17**, 64 (1904); E. A. ATKINSON and

for cobalt, with which it produces a red-brown precipitate. Later, Ilinski and von Knorre[108] recommended it as a reagent for cobalt and ferric iron. There is now a considerable body of literature on the analytical employment of this compound. It has found particular favor for the detection of small amounts of cobalt in the presence of nickel. Ilinski and v. Knorre, and subsequently other workers,[108] observed that this reagent gives precipitates not only with cobalt but, in weakly acidified solutions, with the following metal ions also:

Fe^{III}............................ brown-black
Cu.............................. coffee-brown, with metallic lustre
Zr............................... greenish yellow
Pd.............................. red-brown

Accordingly, 1-nitroso-2-naphthol is a selective reagent, whose value resides in the fact that, with maintenance of certain conditions, it permits the realization of specific tests and quantitative determinations. For example, palladium can be conveniently detected among the noble metals, and cobalt in the ammonium sulfide group, even when copper is present. The latter tests are possible because the tendency to form cobalt nitrosonaphthol is so great that even cobalt phosphate reacts with 1-nitroso-2-naphthol, while the phosphates of iron, uranyl, etc., are not affected. Likewise, copper can be rendered inactive toward this reagent, if it is converted into cuprous iodide by means of iodide and sulfite, which do not affect cobalt. These tests[109] are aided greatly by the light color of the phosphates and cuprous iodide, provided the limiting concentration relationships are favorable. The examples are cited here principally because they are instructive demonstrations of the increase in the selectivity of a test that can be brought about, not by resorting to masking agents, but solely by converting the interfering ionic species into nonreactive, insoluble principal valence compounds.

For many years, 1-nitroso-2-naphthol was used only as a reagent for cobalt and iron. It has acquired further importance since Schmidt[110] proved that it is a sensitive precipitant for palladium. In addition, Bellucci and Savoia[111] found that it precipitates zirconium in acid solution. These salts have the empirical formulas:

$$Co[C_{10}H_6(NO)O]_3 \cdot 2H_2O; \quad Pd[C_{10}H_6(NO)O]_2; \quad ZrO[C_{10}H_6(NO)O]_2$$

E. F. SMITH, J. Am. Chem. Soc. 17, 688 (1895); W. SCHMIDT, Z. anorg. allgem. Chem. 80, 335 (1913); M. WUNDER and V. THÜRINGER, Z. anal. Chem. 52, 737 (1913); L. BELLUCCI and G. SAVOIA, Chem. Abstracts 18, 3333 (1924).

[109] F. FEIGL, Spot Tests, p. 109.

[110] W. SCHMIDT, Z. anorg. allgem. Chem. 80, 335 (1913); M. WUNDER and V. THÜRINGER, Z. anal. Chem. 52, 737 (1913).

[111] L. BELLUCCI and G. SAVOIA, Chem. Abstracts 18, 3333 (1924).

The isomeric 2-nitroso-1-naphthol behaves similarly to 1-nitroso-2-naphthol. The salts have the same composition and, with the exception of the zirconium precipitate, the same colors. According to Bellucci and Savoia (*loc. cit.*) the zirconium salt of 1-nitroso-2-naphthol is greenish-yellow; the isomeric compound is deep red. When dissolved in chloroform, both salts retain their respective colors.

The active salt-forming group that is built into the naphthalene ring of these two reagents is the =C(NO)—C(OH)= group. It is logical to regard the water-insoluble salts as inner complex compounds, because their colors differ from those of the reagents and the respective metal ions, and also because these products are quite soluble in organic liquids. For instance, the cobaltic and ferric salts dissolve fairly well in aniline, phenol, benzene, or carbon disulfide. The ferric salts produce deep brown solutions.

Various views have been advanced regarding the coordination formulas of the inner complex salts of the nitrosoanaphthols. These suggestions will be reviewed critically. Certain conclusions regarding the type of inner complex rings can be drawn from an inspection of the analytical findings with analogously constructed compounds and from a consideration of the relation between atomic grouping and selective actions. The following possibilities occur at once:

(1) The phenolic group is salt-forming, and coordination of the metal atom takes place on the NO group. (See (I) or (II) in which Me = one equivalent of metal);

(2) The NO group enolizes with formation of an *o*-quinone oxime. In this transformation, the =C(NO)—C(OH)= group goes over into the —C(:NOH)—C(:O)— group. The NOH group of the quinone oxime is salt-forming, and coordination of the metal atom occurs on the CO group. In this case, the NOH group as such can be salt-forming, as shown in (III), or it may function in its tautomeric O=N—H form, as shown in (IV):

(I)   (II)   (III)   (IV)
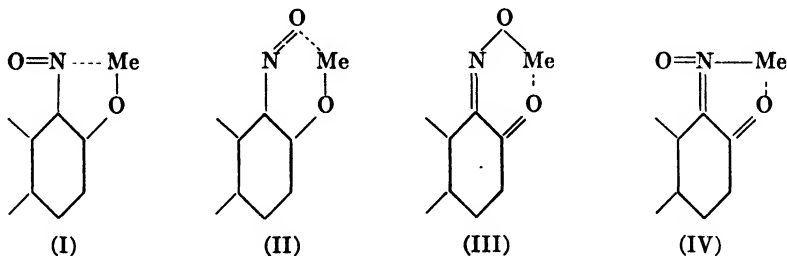
Until recently, it was assumed that 1-nitroso-2-naphthol is salt-forming in the oxime quinone form. The reason for this belief was the

observation that cobalt nitrosonaphthol cannot be precipitated from a strong acid solution, but if the cobalt salt is thrown down from a weakly acidified or neutral solution, the precipitate is stable toward even very strong acids. This finding can be satisfactorily accounted for by postulating the existence of an equilibrium in solutions of the reagent:
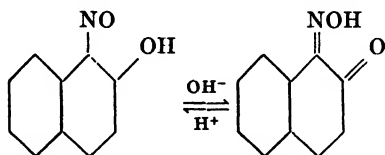
and assuming that only the latter tautomer is consumed in the production of the salt.

Fundamentally, inner complex salts of the oxime quinone form might correspond to either (III) or (IV). However, the latter structure was accepted on the basis of Pfeiffer's studies (see p. 43), which demonstrated that the oxime group of 1,2-dioximes reacts in the tautomeric $O{=}N{-}H$ form. Sarver,[112] and Yoe and Sarver[113] do not accept either (III) or (IV). They base their rejections on the observations of Herfeld and Gerngross,[114] who found that 1-nitro-2-naphthol (V) reacts with cobalt and palladium salts quite like 1-nitroso-2-naphthol. The color of the nitro compounds is the same as that of the corresponding nitroso compounds. These surprising findings are taken by Yoe and Sarver as proof that the metal atom replaces the hydrogen of the phenol group. Consequently, they assume that the phenolic coordination formula (VI) represents the inner complex metal salts of the nitro compound, and accept the analogous phenolic formula (II) for the nitroso compound.
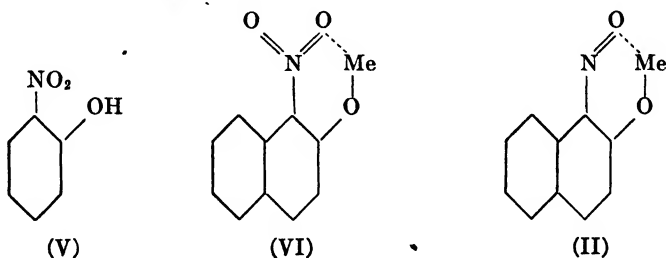
The author cannot subscribe to these conclusions that have been drawn from the behavior of the nitro compound. It seems much more reason-

[112] L. A. SARVER, Ind. Eng. Chem., Anal. Ed. 10, 378 (1938).

[113] J. H. YOE and L. A. SARVER, Organic Analytical Reagents, page 129. New York, 1941.

[114] H. HERFELD and O. GERNGROSS, Z. anal. Chem. 94, 7 (1933).

able to postulate a tautomeric equilibrium in the case of the 1-nitro-2-naphthol. This tautomerism, which is analogous to that assumed for other nitro compounds, leads to an *aci*-nitro (isonitro) form:
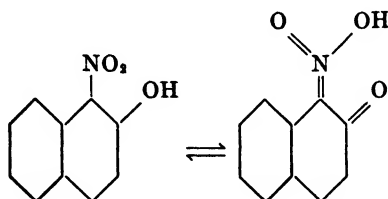
This likewise leads to an orthoquinoid oxime, whose inner complex salts, however, can be formulated solely by (VII). A comparison of (VII) with the corresponding coordination formula (III) of the nitroso compound, shows them to be practically identical as regards the inner complex ring and its attached naphthalene ring:

<center>(VII)   (III)</center>
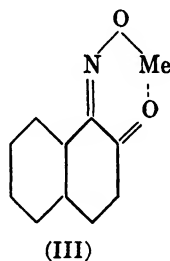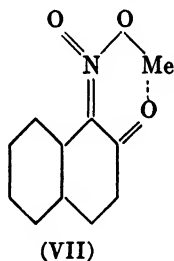
This formulation of the nitroso- and nitronaphthol compounds as salts of enolizable NO or NO_2 groups, respectively, is supported by the behavior of other substituted nitrosonaphthols, which will be considered presently. Another finding, which likewise argues for the reaction of nitrosonaphthols in the oxime form, can be cited. Straus and Ekhard[115] observed that 1-isonitroso-2-ketotetralin (VIII) forms colored precipitates with cobalt and iron salts. This compound

<center>(VIII)</center>
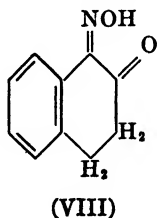
does not occur as an equilibrium mixture of tautomers, but is present solely as the *o*-quinone oxime. The color of the precipitates and their

[115] F. STRAUS and W. EKHARD, *Ann.* **444**, 154 (1924).

acid-resistance are, of course, different from those derived from the nitrosonaphthols, because of the ligation of the active group in an aliphatic ring.

The recognition of the active group in 1-nitroso-2-naphthol has led, through the introduction of solubility-promoting groups, to water-soluble reagents for cobalt. An excellent example is 1-nitroso-2-naphthol-3,6-disodium sulfonate (IX) recommended by van Klooster.[116] This reagent, also known as nitroso-R-salt, gives a red soluble cobalt salt (X), that lends itself well to the colorimetric determination of small amounts of cobalt.

(IX)   (X)
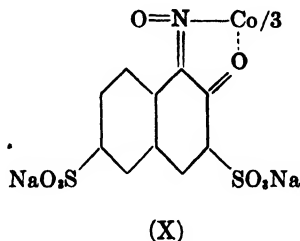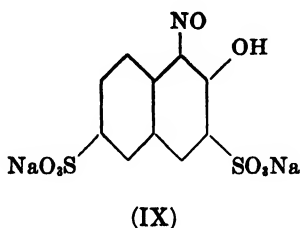
van Klooster prescribes buffering by acetate before the addition of the reagent, otherwise the color does not develop. Nickel and iron salts also give color reactions with this reagent, but this interference can be safely eliminated i.e., without decrease of the cobalt color, by adding strong nitric acid after the cobalt color has developed. These reaction conditions are excellent proof that an enolization of the NO group to the NOH group is essential to the formation of the cobalt salt because the phenolic OH group cannot be salt-forming, since it remains unaltered when the solution is buffered. In view of the marked acid-stability of the insoluble cobalt nitrosonaphtholate once the salt has been formed, the argument may be advanced that this fact is not necessarily an infallible proof that the reagent functions in its tautomeric NOH form. Instead, the aging of the precipitate might be rapid. However, this type of objection cannot be offered in the case of the water-soluble cobalt salt of nitroso-R-salt. Consequently, even though buffering is a necessary preliminary to the formation of this cobalt salt, which subsequently displays resistance to acids, the only explanation remaining is that an enolization of the NO group is brought about by the buffering. The analogous constitutions of the nitroso-naphthols and nitroso-R-salt doubtless justify the assumption that the inner complex rings containing salt-forming NOH groups are similarly constructed in both cases.

[116] H. S. van Klooster, J. Am. Chem. Soc. 43, 746 (1921).

Nitroso-R-salt produces water-soluble inner complex compounds in all concentrations of Co^{++}, Cu^{++}, and Fe^{++} ions. The behavior of 2-nitroso-1-naphthol-4-sulfonic acid (I) is somewhat different. Sarver (*loc. cit.*) found that this water-soluble reagent produces precipitates from neutral concentrated solutions of the ions just mentioned: Co (red); Cu (orange); Fe (green). Corresponding colorations are formed in solutions of intermediate concentration, and at dilutions up to 1:20,-000,000. Accordingly, a comparison of 1-nitroso-2-naphthol-3,6-disulfonic acid with 2-nitroso-1-naphthol-4-sulfonic acid plainly reveals the solubility-promoting action of SO_3H groups on both reagent and reaction product, as well as the enhancement of the solubility of the salts with increase in the number of SO_3H groups. The metal salts of the two sulfonated nitrosonaphthols probably are compounds with inner complex anions analogous to those present in the soluble metal salts of sulfonated 8-hydroxyquinoline (ferron) discussed on p. 187ff. The salts of the sulfonated nitrosonaphthols conform to the solubility rule governing inner complex compounds (see p. 409). Because of their free SO_3H groups they accordingly are not soluble in organic liquids, as opposed to the salts of the non-sulfonated nitrosonaphthols which do dissolve. Therefore, the former salts cannot be extracted by organic solvents from their water solutions or suspensions.

Brenner[117] was the first to study a nitrosonaphthol which was rendered water-soluble by the introduction of SO_3H groups. To be sure, his work was not with sulfonated nitrosonaphthol (I), but with nitrosochromotropic acid, which is 2-nitroso-1,8-dihydroxy-3,6-naphthalene disulfonic acid (II):

(I)   (II)
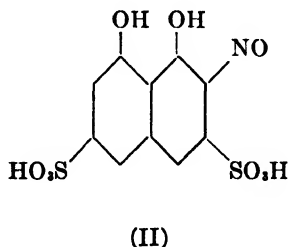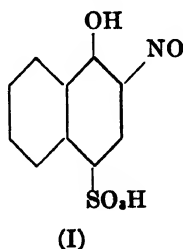
There is a definite possibility that both of the *peri*-situated OH groups of (II) may function as salt-forming or coordinating groups, and consequently its salts may have another structure. Evidence in favor of this possibility is the fact that addition of this reagent to ammoniacal cobalt solutions produces a blue coloration, *i.e.*, a color which differs from that obtained with any of the preceding nitroso compounds. The maximum

[117] C. BRENNER, *Helv. Chim. Acta* **3**, 90 (1920).

intensity of this color is attained at the ratio: 1 Co: 1 chromotropic acid. A brown coloration is obtained in weak caustic alkali solutions at the ratio: 1 Co: 6 chromotropic acid. Therefore, the former case may involve divalent, and the latter trivalent cobalt. These color reactions can be applied in micro determinations of cobalt, and also of copper, which likewise gives a colored, soluble salt with this reagent.

The cobalt salts of nitrosonaphthols may contain the metal in the divalent as well as the trivalent condition. This observation was made by Ilinski (loc. cit.), who stated that the cobaltic salt of 1-nitroso-2-naphthol is purple red, while its cobaltous salt is brown-red. However, analytical data and different colors are not unassailable proofs of the presence of trivalent cobalt. A compound of divalent cobalt that contains one molecule of coordinated 1-nitroso-2-naphthol gives the same analytical figures as a compound containing trivalent cobalt, because the absence of one hydrogen atom will not be disclosed by the analysis. The questions as to whether di- or trivalent cobalt is present, and whether pure precipitates can be obtained, are important points with respect to the use of 1-nitroso-2-naphthol in the gravimetric determination of cobalt. For a long time, it was not possible to utilize the precipitate as the final weighing form; it was not homogeneous. The variation in composition presumably arose from differences in the valence of the cobalt. At the author's suggestion, Mayr[118] made a study designed to determine definitely the presence of trivalent cobalt, and, in case this was established, to discover the conditions necessary to produce a pure precipitate. He found that solutions of $Na_3[Co(NO_2)_6]$, in which the cobalt unquestionably is trivalent, on treatment with the reagent give a purple-red precipitate, whose composition is exactly that demanded by cobaltic nitrosonaphtholate. He also found that cobaltic acetate solutions, which are readily prepared by dissolving $Co(OH)_3$ in strong acetic acid, give pure precipitates of cobaltic nitrosonaphtholate, that can be dried at 130°C. and then weighed.[119] These definite findings and the

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[118] C. MAYR and F. FEIGL, Z. anal. Chem. **90**, 15 (1932).

[119] In any case, there is an extraordinarily great tendency to form cobaltic nitrosonaphthol. This was demonstrated very definitely by G. T. MORGAN and J. D. M. SMITH [J. Chem. Soc. **119**, 704 (1921)] who studied the behavior of hexammine cobaltic chloride (luteo chloride) $[Co(NH_3)_6]Cl_3$ toward a weakly ammoniacal solution of α-nitroso-β-naphthol. The dark green precipitate $[Co(NH_3)_6][C_{10}H_6O(NO)]_3$ is soluble in alkali. This product is a luteo salt of the nitrosonaphthol and is not an inner complex salt. If it is suspended in water and warmed gently, or if a weakly ammoniacal solution of the nitrosonaphthol is boiled with the original luteo salt, brown-red alkali-stable, inner complex cobaltic nitrosonaphthol results. This transformation is all the more remarkable because the $[Co(NH_3)_6]^{+++}$ ions produced by the original luteo salt are extremely stable and are not decomposed either by acids or

analytically applicable precipitation of the cobaltic salt of 1-nitroso-2-naphthol do not, of course, guarantee that all derivatives of this reagent will produce trivalent cobalt salts.   However, reasoning by analogy leads to the conclusion that this possibility is fundamentally sound.[119a]   It should be noted that divalent cobalt is oxidized to the trivalent condition at the expense of the nitrosonaphthol.   This agrees closely with the view (see p. 255) that 1-nitroso-2-naphthol reacts in its isomeric oxime form. The latter, as an *o*-quinoid, can function as an oxidizing agent.   There is the further possibility that autoxidation of the cobalt may occur.   This action of the oxygen of the air is particularly likely in neutral or alkaline reaction media (see p. 234).

The effect of introducing other groups into organic reagents that owe their selective action to a salt-forming group is often of considerable analytical interest, since the salts of these derivatives may exhibit more advantageous colors or solubilities.   An inspection of the structural formula of 1-nitroso-2-naphthol shows that this compound can be regarded as a derivative of the parent substance *o*-nitrosophenol (I). Baudisch[120] described a simple method of obtaining stable solutions of the latter in petroleum ether.   This advance enabled Cronheim[121] to study its analytical behavior.   His findings deserve consideration both from the viewpoint of the problems discussed in this chapter, and because of their analytical implications.   The salt-forming ability of *o*-nitrosophenol was found to be less selective than that of the nitrosonaphthols and their sulfonated derivatives; it reacts with a greater variety of metal ions than they do.   Colored water-soluble compounds are formed with colorless as well as with colored metal ions.   The inner complex character of these products is disclosed by their more intense color and also by their solubility in organic liquids, such as ether and chloroform.   The

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dilute alkali.   Consequently, a quite stable complex ion is broken down as a result of the formation of an inner complex.

[119a] I. M. KOLTHOFF and A. LANGER, *J. Am. Chem. Soc.* **62**, 3172 (1940) studied the precipitation of cobalt with *α*-nitroso-*β*-naphthol by means of amperometric titration.   They found that red-brown $Co[C_{10}H_6O(NO)]_2$ is precipitated from a neutral solution by the potassium salt of the reagent.   A purple-red precipitate, $Co[C_{10}H_6O(NO)]_2 \cdot 2C_{10}H_7O(NO)$, is formed from a buffered acetic acid solution. These workers therefore conclude, in opposition to Feigl and Mayr (*loc. cit.*) that no $Co[C_{10}H_6O(NO)]_3$ is precipitated from acetic acid solution.   Accordingly, the question as to whether cobalt is trivalent in nitrosonaphtholates requires further study. The writer believes that the product obtained by Kolthoff and Langer from weak acetic solution can also be regarded as Co[III] salt with one molecule of coordinated nitrosonaphthol.

[120] O. BAUDISCH, *J. Am. Chem. Soc.* **63**, 622 (1941); *Science* **92**, 336 (1940).

[121] G. CRONHEIM, *Ind. Eng. Chem., Anal. Ed.* **14**, 445 (1942).

salts of o-nitrosophenol can be divided into two classes on the basis of their behavior toward petroleum ether:

Soluble		Insoluble	
Co	greyish-brown	Cu	reddish-violet
Pd	green	Hg	reddish-violet
Fe^{III}	brown	Ni	red
		Zn	red
		Fe^{II}	green

This classification is rather remarkable and has considerable interest from the analytical viewpoint. The foregoing colored salts can be formed by merely shaking a neutral or very slightly acidified aqueous solution of the metal salt with a petroleum ether solution of o-nitrosophenol. Therefore, the extremely small amount of the reagent that passes from the petroleum ether into the water (partition equilibrium) suffices to exceed the ion-product of the inner complex salt. Hence, tests with o-nitrosophenol are extremely sensitive; they give positive results at dilutions as extreme as 1:10,000,000. Cronheim showed that this reagent gives excellent results in colorimetric determinations of cobalt and iron. The latter finding is especially interesting because, after any necessary reduction, 2γ iron in 50 ml. can be handled successfully.[122] The preceding list shows that ferrous nitrosophenolate is not soluble in petroleum ether. Consequently, after the test solution is shaken with the reagent solution, the product stays in the water layer, and the excess of reagent remains in the petroleum ether layer. This is the only known instance of this type of colorimetric procedure, in which a colored product and a colored reagent are separated. Cronheim (loc. cit.) believed the metal salts of o-nitrosophenol to be inner complex salts, but he did not suggest any coordination formulas for them. By analogy with the inner complex salts of 1-nitroso-2-naphthol, the orthoquinoid formula (II) or (IIa) seems likely:
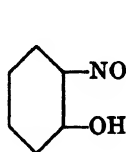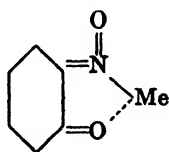
Me = 1 equiv.

(I)   (II)   (IIa)
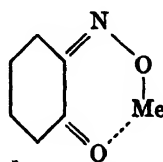
The fact that the inner complex salts of o-nitrosophenol are soluble in water is remarkable, because this usually is not true of inner complex salts containing the heavy metal in the cationic component. The

[122] G. Cronheim and W. Wink, Ind. Eng. Chem., Anal. Ed. 14, 447 (1942).

insolubility of the inner complex salts of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol, accordingly, is a clear manifestation of a weighting effect of the naphthalene ring (see Chapter IX). Since the procedure developed by Baudisch (*loc. cit.*) now makes it possible to prepare substituted *o*-nitrosophenols, it may be anticipated that comparisons of the salts of *o*-nitrosophenol and of its substitution products will be made. The findings should give interesting insights regarding the effect of substituents on the active group, and on the properties of the corresponding salts.

Selective Actions of Nitrosoarylhydroxylamines (Cupferron and Neocupferron)

Shortly after Tschugaeff-Kraut-Brunck (1905–1907) recommended dimethylglyoxime as a specific reagent for nickel, Baudisch[123] discovered a compound that quantitatively precipitates ferric iron and copper from mineral acid solutions. He appropriately named this reagent "cupferron." It is the water-soluble ammonium salt of nitrosophenylhydroxylamine (I). When dissolved in chloroform, the whitish-gray copper compound gives a bright yellow solution, and the brown-yellow ferric compound a deep red solution. This behavior reveals the character of these compounds as inner complex salts that may be represented by (II) and (III), respectively:
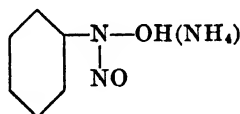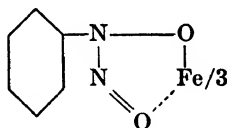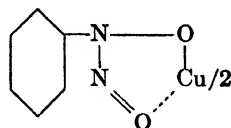
(I)   (II)   (III)

Many texts, without adequate justification, give the formula

$$C_6H_5{-}(NO){=}NOH$$

for nitrosophenylhydroxylamine (and its inner complex salts).[123a] This formula is isomeric with (I). A real argument favoring the possibility of nitrosophenylhydroxylamine reacting in two forms that are isomeric with each other is the fact that nitrosobenzene is produced when this compound decomposes. The assumption of an isomerism finds further support in the fact that when the copper and iron salts are dissolved in organic

[123] O. BAUDISCH, *Chem. Ztg.* **33**, 1298 (1909).
[123a] F. J. WELCHER, *op. cit.*, Vol. III, pp. 155, 355 regards the as yet not fully proven form $C_6H_5{-}(NO){=}NOH$ as an oxime form and hence places cupferron in the class of oximes. This is not legitimate, because the accepted organic nomenclature requires that oximes contain the NOH group doubly bonded to a C atom.

liquids the colors of the solutions differ from those of the solid salts. It is well established that such extensive color differences of compounds in the solid and dissolved states frequently are due to differences in constitution.

When cupferron was introduced as a reagent by Baudisch it created a mild sensation because it was assumed, at first, that this organic precipitant exercises a selective action on iron and copper in acid solution. It became the subject of many investigations. Although it soon became evident that its precipitating action is not restricted to copper and iron, the reagent has acquired permanent value as an aid in separating certain metals. Many other metals are quantitatively precipitated from mineral acid solution by cupferron, and especially, with the exception of aluminum and chromium, almost all the 3- to 5-valent metals that form insoluble hydrous oxides. Excellent examples of its value are the elegant separation of titanium from aluminum and chromium, and the precipitability of zirconium from strong sulfuric acid solutions. This latter instance demonstrates the extremely low solubility of the zirconium-cupferron complex, since many precipitations of zirconium salts from sulfuric acid solutions are masked because of the presence of complex zirconium sulfuric acid or its ions (see p. 72).

When the metal salts of cupferron are precipitated from mineral acid solutions, there is always coprecipitation of nitrosophenylhydroxylamine. It is not feasible to wash out this water-insoluble "free acid" with an organic solvent or ammonia, because the metal cupferronate precipitate is then partly dissolved, or undergoes partial decomposition into a hydrous oxide. Consequently, cupferronates cannot be used as final weighing forms, and they serve only for purposes of precipitation and separation. The low percentage content of metal, which is exploited in the case of so many other organic precipitants, unfortunately offers no particular advantage here. In quantitative work, it is necessary to ignite the precipitate to the oxide. If the precipitation is carried out in acetic acid solution the decomposition of the ammonium salt of nitrosophenylhydroxylamine into the free acid is slight. The many analytical uses of cupferron[124] will not be discussed because they contribute little to the present discussion of the relations between atomic groupings and selective action. On the other hand, the homologues of cupferron have some characteristics that are not only striking but also quite instructive

[124] Data and references to the literature can be found in W. PRODINGER, Organic Reagents Used in Quantitative Inorganic Analysis (translated by S. Holmes), Elsevier Publishing Co., New York, 1940, pages 72–81; J. H. YOE and L. A. SARVER, Organic Analytical Reagents, J. Wiley and Sons, New York, 1941, page 220; G. F. SMITH, Cupferron and Neocupferron, G. F. Smith Chemical Co., Columbus, 1938.

with regard to the points being emphasized here. These findings are taken from the thorough studies by Baudisch and his collaborators.[125]

The active, inner complex salt-forming group in cupferron is $-N\underset{NO}{\overset{OH}{<}}$.

Since the NOH group of the parent hydroxylamine shows an acidic character only toward alkali metals, it must be assumed that the acidity of cupferron is caused by the influence of the negative C_6H_5 and NO groups. The fact that aliphatic nitrosohydroxylamines have no precipitating action is in line with this reasoning. On the other hand, the quantitative precipitability of iron and copper is retained when the group cited above is bound to aromatic radicals other than C_6H_5. The following pertinent examples of ammonium salts are taken from the findings of Baudisch.
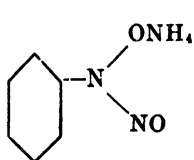
(I) Nitrosophenyl-
hydroxylamine
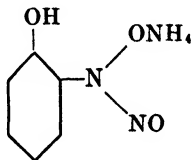
(II) o-Hydroxynitroso-
phenylhydroxylamine
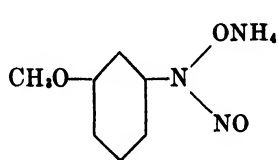
(III) m-Methoxy-
nitrosophenyl-
hydroxylamine
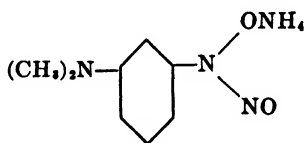
(IV) m-Dimethylaminonitroso-
phenylhydroxylamine
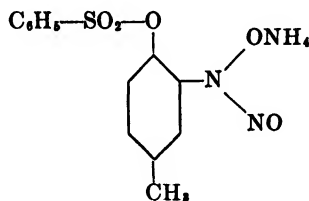
(V) p-Toluene sulfonic
acid-o-nitrosohydroxyl-
amine phenyl ester
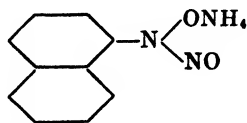
(VI) α-Nitrosonaphthyl-
hydroxylamine

[125] O. Baudisch and N. Karzeff, Ber. 45, 1164 (1912); O. Baudisch and R. Fürst, ibid. 48, 1665 (1915); O. Baudisch, H. Gurewitsch and S. Rothschild, ibid. 49, 180 (1916); O. Baudisch, A. E. Pistor and B. Silberblatt, ibid. 49, 191 (1916); O. Baudisch and H. Rom, ibid. 49, 203 (1916); O. Baudisch, ibid. 49, 172 (1916).

The colors of the copper and ferric salts of (I) to (VI), and also the colors of the respective chloroform solutions of these salts, are given in Table VIII.

TABLE VIII

Nitrosoarylhydroxylamine Reactions

Nitroso-arylhydro-xylamine	Copper salt		Ferric salt	
	Solid	In chloroform	Solid	In chloroform
(I)	Whitish grey	Bright yellow	Yellow	Red
(II)	Grey	Blue-green	Yellow	Red
(III)	Light grey	Dark blue	Yellow-brown	Deep red
(IV)	Yellowish-green	Dark blue (slightly soluble)	Dark brown	Deep red
(V)	Grey-blue	Blue	Yellow	Deep red
(VI)	Grey	Yellow	Yellow-brown	Red

These findings show that the introduction of substituents into the phenyl radical of nitrosophenylhydroxylamine does not change the precipitation action, but marked color changes result, particularly in the light colored copper salts. As was expected, the effect is most decided in the case of the chromophoric $N(CH_3)_2$ group, and appears even in the color of the ferric salt. Furthermore, the chloroform solutions of these inner complex copper and iron salts demonstrate, without exception, that when dissolved the color of the solution in an organic liquid is by no means necessarily identical with that of the solid (see p. 277, note 160). This fact has analytical interest but, in addition, it surely is of general significance with respect to the constitution and condition of compounds in the solid and dissolved states.

Cupferron produces precipitates, in neutral solution, with many metal salts, but no attempt has been made, as yet, to use these observations for analytical purposes. Substituents in the phenyl radical appear to influence the solubility characteristics of the various precipitation products of cupferron derivatives. For instance, Baudisch states that (V), which gives a clear solution in distilled water, produces a precipitate in well water. This result is probably due to the formation of calcium and magnesium salts and may be of interest in hardness determinations. A weighting effect by the p-toluenesulfonic acid radical is possibly operative here. Baudisch and Holmes[126] have reported some interesting findings obtained with the ammonium salt of 1-nitrosonaphthylhydroxylamine (neocupferron, VI). Its uranium, neodymium, and cadmium salts

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[126] O. BAUDISCH and S. HOLMES, *Z. anal. Chem.* **119**, 16 (1940).

are soluble in organic liquids, in contrast with the corresponding cupferron precipitates. Perhaps the latter are mixtures with the basic salts. Neocupferron produces a discernible precipitate with much smaller quantities of iron than are revealed by cupferron; for instance, 5 mg. of iron per liter gives a fairly voluminous precipitate. Here again there is a marked weighting effect, secured in this case by substituting the naphthyl for the phenyl radical bound to the active group. Baudisch and Holmes have therefore recommended the use of neocupferron to precipitate small amounts of iron or copper directly from water, without preliminary evaporation. They (*loc. cit.*) have described a preparative procedure, which doubtless can be used to bind the active $N{\diagup OH \atop \diagdown NO}$ group to an anthracene group. If this were accomplished, interesting data regarding weighting effects (see Chapter IX) could be secured from a comparison of the precipitation sensitivities of the C_6H_5, $C_{10}H_7$, and $C_{14}H_9$ compounds. Perhaps a nitrosoarylhydroxylamine with a particularly high precipitating action might be developed from this study.

Shome,[127] proceeding from the assumption that the $C_6H_5—\overset{\displaystyle |}{N}—OH$ group of nitrosophenylhydroxylamine is salt-forming, studied the behavior of NO-free compounds of the general formula $C_6H_5—\overset{\displaystyle R}{\underset{\displaystyle |}{N}}—OH$ with the hope of producing derivatives of phenylhydroxylamine that would be more selective in their precipitating actions than cupferron. The radicals (R) introduced into the phenylhydroxylamine, and bound to nitrogen, were: CHO, $COCH_3$, COC_6H_5, $CONH_2$, $CONHC_6H_5$, $CSNH_2$, $CSNHC_6H_5$, $CSNHCH_2CH:CH_2$. The compounds containing the groups COC_6H_5, $CSNH_2$, and $CSNHC_6H_5$ seem to evidence certain advantages, provided particular pH values are maintained. No statements have appeared as yet regarding the applicability of these compounds in qualitative and quantitative analysis.

The Copper-Specific Group $\diagup^{\diagdown}{C—C— \atop |\ \ ||}\ _{OH\ NOH}$
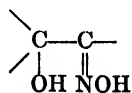
The α-acyloinoximes, have been shown by systematic tests[128] to react toward cupric salts as dibasic acids. The green products do not dissolve in water. In view of the comments on p. 43 concerning the salt-

[127] S. C. SHOME, *Chem. Abstracts*, **40**, 7047 (1946).
[128] F. FEIGL, G. SICHER and O. SINGER, *Ber.* **58**, 2294 (1925).

formation of oximes, these copper compounds should be formulated:

$$\begin{array}{ccc} R\!-\!CH\!-\!C\!-\!R' \\ | \quad \| \\ O \quad NO \\ \diagdown \diagup \\ Cu \end{array}$$
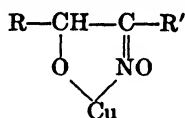
The aliphatic dibasic group $\rangle C(OH)\!-\!C(\!:\!NOH)\!-$ is the copper-specific group of the acyloinoximes. It alone determines the water-insolubility and the color of these copper salts, because a variation of the radicals R and R′ produces no change in these respects. The radicals make their effects evident only in the behavior of the copper salts toward ammonia. The salts are insoluble in ammonia (or have no capacity for adding ammonia) if R and R′ are able to saturate the copper atom coordinatively, whereby the corresponding copper compounds acquire the character of inner complex salts. Aromatic radicals, such as phenyl, furoyl, and benzyl are always suitable for this, and there is no difference in this respect between symmetrical and unsymmetrical acyloinoximes. Substitution in the C_6H_5 group of benzoinoxime

$$C_6H_5\!-\!CH(ON)\!-\!C(NOH)\!-\!C_6H_5$$
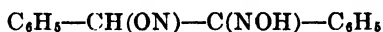
by methoxy-, isopropyl- or methylenedioxy- groups, for instance, has no effect, and the behavior of phenyloxethenylamidoxime,

$$C_6H_6\!-\!CH(OH\!-\!C(NOH)(NH_2)$$
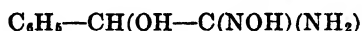
that likewise forms a copper salt insoluble in ammonia, shows that an NH_2 group obviously can play the same coordinative role as a C_6H_5 group. Among the aliphatic acyloinoximes there are compounds such as valeroin-, capronoin-, and oenanthoinoxime, whose copper salts likewise are difficulty soluble in ammonia. Consequently, multi-membered aliphatic radicals appear to have coordinative capacities. In any event, the insolubility of copper acyloinoximes in ammonia is not due to a weighting effect of the radicals R and R′, but can be ascribed solely to their coordination ability. This is evidenced in the behavior of phenyl- and benzylbenzoinoxime,

$$(C_6H_5)_2C(OH)\!-\!C(NOH)\!-\!C_6H_5 \text{ and } (C_6H_5)(C_6H_5CH_2)C(OH)\!-\!C(NOH)\!-\!C_6H_5$$

Their copper salts are soluble in ammonia, despite the high atomicity of the anionic constituent, whereas other copper salts with a smaller anionic part are insoluble in ammonia. This solubility in ammonia can be interpreted by assuming a compensation of affinity between the aromatic radicals bound to the same carbon atom, whereby each loses its ability to saturate the copper atom coordinatively.

The copper specificity of the group $-CH(OH)\!-\!C(\!:\!NOH)\!-$ is

retained even after inclusion in a cyclic ring. This is shown[128a] by the green water-insoluble copper salt of o-cyclohexanolonoxime:

$$
\begin{array}{c}
O{=}N{-\!-\!-\!-\!-}Cu \\
\ \ \| \qquad\quad \ | \\
\ \ C \qquad\quad \ O \\
H_2C \diagup\ \ \diagdown\ C{-}H \\
H_2C \qquad\quad CH_2 \\
\ \ \diagdown\ \ C \ \diagup \\
\ \ \ \ H_2
\end{array}
$$
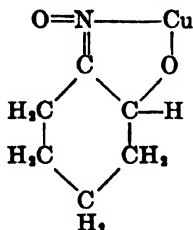
As was to be expected, this copper salt is soluble in ammonia, since the cyclohexane ring is completely saturated and thus becomes incapable of being coordinated on the copper atom.

Hofmann and Küspert[129] were the first to show that a ring system that is unsaturated because of double bonds is capable of coordination; they worked with $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$. A study of the salt-forming ability of the phenylazoaldoximes, $R{-}C(NOH){-}N{=}N{-}C_6H_5$, with copper, showed that in these cases also the green copper salts are insoluble in ammonia and soluble in organic solvents only when R is aromatic or if it is an aliphatic radical with more than four carbon atoms.[130]

If insolubility and complex formation in the copper salts of acyloin-oximes are to be ascribed to different group effects, then the group $-CH(OH)\cdot C(:NOH)-$ must be considered in the formation of insoluble salts, but the two radicals attached to it become responsible for complex formation. The quantitative precipitability of copper from ammoniacal solutions by means of benzoinoxime ("cupron") is specific, and clearly shows the dependence of specific action on definite group effects.

This dependence is exhibited also in the behavior of the oximes of methylacetonylcarbinol, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot C(:NOH) \cdot CH_3$, and of chloralacetophenone, $CCl_3 \cdot CH(OH) \cdot CH_2 \cdot C(:NOH) \cdot C_6H_5$. These compounds are not capable of forming water-insoluble copper salts,[131] a proof that the five-membered ring closed with principal valences is

$$
\begin{array}{c}
\diagdown \\
\ \ C{-\!-\!-}C{-} \\
\diagup\ | \qquad \| \\
\ \ O \quad\ NO \\
\ \ \diagdown\ \diagup \\
\ \ \ Cu
\end{array}
$$
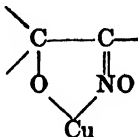
necessary for the specific action.

[128a] F. FEIGL and P. KRUMHOLZ, unpublished studies.

[129] K. HOFMANN and F. KÜSPERT, *Z. anorg. allgem. Chem.*, **15**, 204 (1897).

[130] F. FEIGL, *Oesterr. Chem. Ztg.* **30**, 13 (1927).

[131] F. FEIGL and A. BONDI, *Ber.* **64**, 2819 (1931).

Under special conditions, Co^{++}, Ni^{++}, Pd^{++}, and Pt^{++} also form compounds with benzoinoxime, in which, however, in contrast to its behavior with copper, it acts as a monobasic acid.[132] Knowles[133] found that benzoinoxime forms precipitates with molybdates, tungstates, vanadates, and uranyl salts in mineral acid solutions.   The structure of these products is entirely different from that of Cu benzoinoximate, which is formed in ammoniacal solution.   Possibly the compounds separating from acid solutions are heteropolyacids (see p. 39) containing the metal acid united with the acidic benzoinoxime.   However, it is also possible that esters of the metal acids with benzoinoxime are formed through the activity of the alcoholic OH group of the benzoinoxime (compare the statements regarding reaction of the metal acids with oxine on p. 194). Knowles showed that the precipitation of molybdate with benzoinoxime in acid solution, followed by conversion to MoO_3 by ignition, can be used for the quantitative determination of molybdenum.   Yagoda and Fales[134] report that tungstate can be handled analogously.

The ability of acyloinoximes to form salts is also greatly dependent on their configuration.   β-Benzoinoxime

$$C_6H_5—CH——C—C_6H_5$$
$$\underset{OH}{|}\qquad\underset{HON}{\|}$$
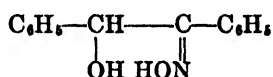
forms a water-insoluble copper salt whose properties are quite different from those of the copper salt of α-benzoinoxime.   It is dirty brown, easily soluble in dilute ammonia, and consequently is probably differently constituted than the green copper salt of α-benzoinoxime.[135]

It is remarkable that the alcoholic OH-group in acyloinoximes has its normally weak acidic character strengthened by the proximity of the NOH group.   Obviously, this effect is connected with the ring closure accompanying salt-formation.   An analogous case was found in the behavior of pyrrole-α-aldoxime (I).[136]   It, or its substitution products,[137] react toward cupric solutions as dibasic acids and form green amorphous salts of the structure (II):

[132] J. Jennings and co-workers, J. Chem. Soc. 1935, 818.

[133] H. Knowles, Bur. Standards J. Research, 9, 1 (1932).

[134] H. Yagoda and H. A. Fales, J. Am. Chem. Soc. 60, 640 (1938).

[135] According to studies by A. Bondi; see also J. Meisenheimer and W. Theilacker in K. Freudenberg, Stereochemie, p. 1019. Leipsic and Vienna, 1933.

[136] B. Emmert, K. Diehl and F. Gollwitzer, Ber. 62, 1735 (1929).

[137] H. Fischer and Z. Csukás, Ann. 508, 172 (1934).

HC——CH
HC   C—CH=NOH
   NH

(I)

HC———CH
HC   C‑ ‑CH
   N
     Cu—N=O
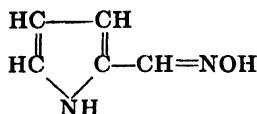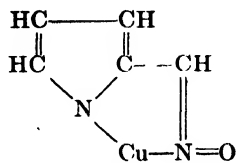
(II)

A certain limitation must be applied to the preceding statement regarding an acidifying effect of the NOH group on α-situated OH and NH groups in α-acyloinoximes and pyrrole α-aldoximes. All available experience indicates that this effect is exhibited solely in the ability to form salts with copper. Probably, this is the basis of the specific precipitating action of the acyloinoximes.

The Nickel and Palladium Precipitating Group   —C—C— / HON NOH

Not only the Tschugaeff reagent,[138] dimethylglyoxime (I), but also numerous other α-dioximes[139] of the general structure (II) react with nickel salts to form colored, usually red, precipitates. These products can be regarded as inner complex compounds of the structure (III):

H₃C—C——C—CH₃
   HON NOH

(I)

R—C——C—R₁
  HON NOH

(II)

R—C———C—R₁
O=N   NOH
    Ni
    ——
    2
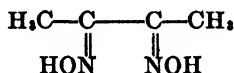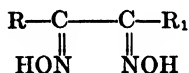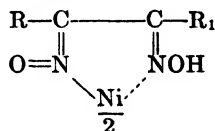
(III)

This coordination formula of the nickel dioxime compounds was advanced by Pfeiffer[140] on the basis of the steric relations established by Meisenheimer for α-dioximes.[141] At the time of Tschugaeff's work, the α-dioximes that react with nickel were quite generally supposed to be *syn* compounds (a). Consequently he assigned the ring structure (b) to nickel diacetyl dioxime:

—C————C—
 NOH HON

(a)

H₃C—C——C—CH₃
   N   NOH
   O——Ni/2
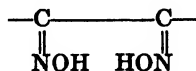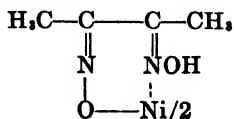
(b)

[138] L. TSCHUGAEFF, *Z. anorg. allgem. Chem.* **46**, 144 (1905); *Ber.* **41**, 2219 (1908).

[139] See especially G. PONZIO, *Chem. Abstracts* from 1922 on.

[140] P. PFEIFFER, *Ber.* **63**, 1811 (1930); compare also P. PFEIFFER and I. RICHARZ, *ibid.* **61**, 105 (1928); P. PFEIFFER and H. BUCHHOLZ, *J. prakt. Chem.* [2] **124**, 133 (1930); W. HIEBER and F. LEUTERT, *Ber.* **62**, 1839 (1929).

[141] See K. FREUDENBERG, Stereochemie, p. 963 ff. Leipsic and Vienna, 1933.

However, Meisenheimer showed that the α-dioximes have the *anti* configuration (I), and this, because of the relative remoteness of the two hydroxyl groups from each other would make the formation of inner complex salts seem improbable. All such difficulty disappears if it is assumed that the oxime salts are derived from the tautomeric amine oxide form, $=$N—H, rather than from the oximino form, $=$NOH. This

$$\overset{\parallel}{\underset{O}{}}$$

concept, due to Pfeiffer, makes it apparent that the *syn* dioximes are entirely incapable of salt-formation, and that *amphi* dioximes form a different type of nickel salts. The following comparison shows that the cause of the different reactivity of the stereoisomeric dioximes is to be sought exclusively in the steric arrangement of the oxime groups:

anti   amphi   syn
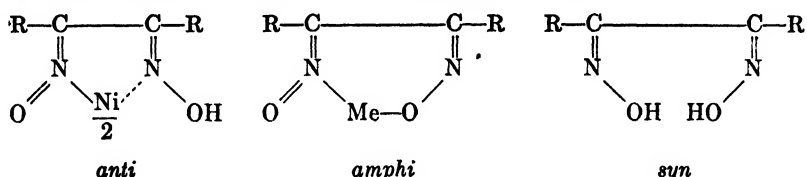
The Pfeiffer formulation of the nickel dioxime salts receives additional support from the finding that the O-methyl ether of dimethylglyoxime (I) forms a red-brown nickel complex salt (II).[142] Hence the hydroxyl group of the second oxime group plays no role in the formation of the complex salt.
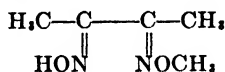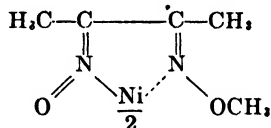
(I)·   (II)

A further argument in favor of this viewpoint is the existence of the two red complex salts[143] in which the second oxime group is replaced by an imino, methylimino, or keto group:
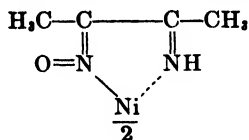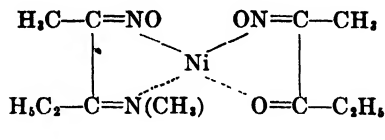
[142] E. THILO and K. FRIEDRICH, *Ber.* **62**, 2998 (1929); compare also O. BRADY and M. MUERS, *J. Chem. Soc.* **133**, 1599 (1930).

[143] P. PFEIFFER, *Ber.* **63**, 1811 (1930).

The ability of the —C(:NOH)—C(:NOH)— group to form a nickel salt is affected permanently by the rest of the constituents of the molecule containing this group. The behavior of oxalenediuramidoxime (I) illustrates this point. According to Feigl and Christiani-Kronwald,[144] this dioxime, in strong ammoniacal solution, loses its ability to form an inner complex nickel salt. It acts as a dibasic acid and forms with Ni++, ions a red-yellow precipitate, whose structure (II) is that of a diammine salt.[145]

$$H_2N—CO—NH—C=NOH$$
$$H_2N—CO—NH—C=NOH$$

$$H_2N—CO—NH—C=NO \quad NH_3$$
$$\hspace{3cm} Ni$$
$$H_2N—CO—NH—C=NO \quad NH_3$$
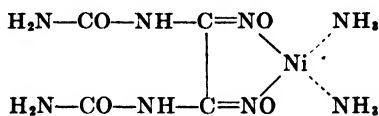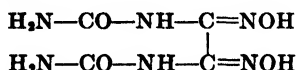
(I)   (II)

The dioxime group likewise loses its selectivity in dioximes of the aromatic orthoquinones. For instance, the dioxime of 1,2-naphthoquinone (III), with almost all metals, forms brown-yellow precipitates in which, in contrast to dimethlyglyoxime, it functions as a dibasic acid. Accordingly, the aromatic ring destroys the nickel-binding action of the two oxime groups, but this is restored if the double bond in the aromatic ring is removed, as in o-cyclohexanedionedioxime (IV). The latter can be viewed as the cyclic analogue of dimethylglyoxime.

NOH

=NOH

(III)

$$CH_2$$
$$H_2C \qquad C=NOH$$
$$H_2C \qquad C=NOH$$
$$CH_2$$
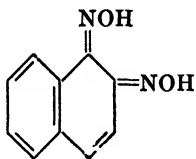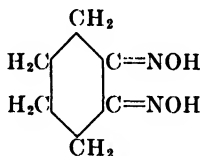
(IV)

(IV)[146] forms a nickel salt that externally cannot be distinguished from nickel dimethylglyoximate. It is produced under the same conditions as the latter, and can also be used in analysis.[146a] •

This dioxime demonstrates the additional fact that the insolubility of the nickel compound is not at all dependent on the insolubility of the dioxime itself in water. Cyclohexanedionedioxime is quite soluble in

[144] F. Feigl and A. Christiani-Kronwald, Z. anal. Chem. **65**, 341 (1925).

[145] R. Chatterjee [J. Indian Chem. Soc. **15**, 608 (1938); Chem. Abstracts **33**, 2841 (1939)] found that oxalenediaminedioxime $H_2N \cdot C(NOH)C(NOH) \cdot NH_2$ in weak ammoniacal solution, forms an inner complex nickel salt. Accordingly, its behavior is analogous to that of dimethylglyoxime.

[146] O. Wallach, Ann. **437**, 148 (1924).

[146a] Compare H. Diehl and coworkers, Analytical Chem. **20**, 458 (1948).

water in contrast to dimethylglyoxime which, as a reagent, must be used in alcoholic solution. Nevertheless, the sensitivity of the nickel test with cyclohexanedionedioxime is twice as great as with dimethylglyoxime. Another somewhat water-soluble (*ca.* 2%) dioxime is α-furildioxime
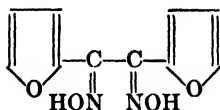
recommended by Soule.[147]

The C(:NOH)—C(:NOH)— group has thus far been regarded as the nickel-binding group, but strictly speaking, this group represents only one particular arrangement of the truly nickel-binding group. The findings of Pfeiffer (see p. 43) give considerable guiding information in this matter. In addition, it may be pointed out that 2-pyridyl methyl ketoxime (I)[148] and 2-pyridyl phenyl ketoxime (II)[149] as well as nitroso-
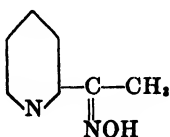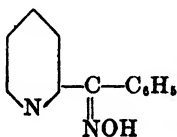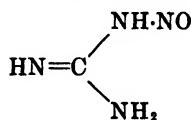
(I)   (II)   (III)

guanidine (III)[150] form characteristic inner complex nickel salts:
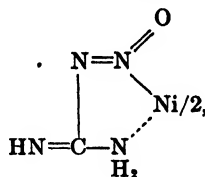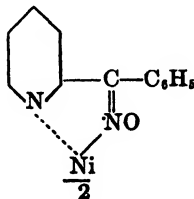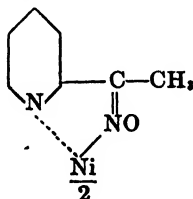
The nitrosoguanidine salt is completely analogous, even in color and solubility relationships, to nickel dimethylglyoximate. These substances and their salts show that the essence of the nickel-binding groups is the union of nickel by one principal and one auxiliary valence to two nitrogen atoms, with resulting development of a five-membered ring.

The behavior of dimethylglyoxime (other dioximes act analogously) toward metal ions furnishes an excellent illustration of the dependence of the activity of the —C(:NOH)—C(:NOH)— (dioxime) group on the reaction conditions. Dimethylglyoxime is a specific reagent for the

[147] A. Soule, *J. Am. Chem. Soc.* **47**, 981 (1925).
[148] L. Tschugaeff, *Ber.* **39**, 3382 (1906).
[149] B. Emmert and K. Diehl, *Ber.* **62**, 1738 (1929).
[150] J. Thiele, *Ann.* **273**, 133 (1893).

precipitation, at room temperature, of nickel from ammoniacal solutions that also, when necessary, contain alkaline tartrate to prevent the precipitation of hydrous ferric oxide, *etc.* Under these conditions, no other metal ions are precipitated.[151] Palladium as well as nickel, can be precipitated from solutions containing acetic acid. The former[152] comes down as an egg-yellow crystalline precipitate, whose formula is analogous to that of the inner complex red Ni dimethylglyoximate. However, the same palladium salt can be produced from weak mineral acid solution, *i.e.*, under conditions at which no nickel precipitate can be formed. Accordingly, these precipitating actions function at pH values so widely separated that dimethylglyoxime can be designated as a special reagent, both for nickel and for palladium.[153]

The precipitating actions of dimethylglyoxime should not lead to the conclusion that its oxime groups react solely with Ni^{++} and Pd^{++} ions. On the contrary, this reagent can react also with Cu^{++}, Fe^{++}, and Co^{++}

[151] This statement requires certain qualifications. It is incorrectly recorded in the literature that Pd dimethylglyoximate is soluble in ammonia, and consequently, no precipitate appears when dimethylglyoxime is added to an ammoniacal palladium solution. Unpublished studies with H. A. Suter have revealed the following. No precipitate appears, even after 3–4 hours standing at room temperature, when the reagent is added to a strong ammoniacal solution containing colorless $[Pd(NH_3)_2]^{++}$ ions. On longer standing, and particularly on warming, the solution turns yellow, and an incomplete precipitation of Pd dimethylgyloximate ensues. Palladium can be precipitated more rapidly, but again only incompletely, from weakly ammoniacal solutions, especially if ammonium salts are present. The compound can be isolated (for instance, by precipitation from an acid solution) and, after washing, is only slightly soluble in ammonia even on warming. The solution is yellow. A further qualification of the precipitation specificity of dimethylglyoxime in ammoniacal solution is necessary when the simultaneous presence of Fe^{+++} and Co^{++} ions must be taken into account. At higher concentrations of these ions in a solution that also contains tartrate, brown-red $FeCoC_{12}H_{19}N_6O_6$ is precipitated, even though these ions, if alone are not precipitated. The studies of G. Weeldenburg cited on p. 83, as well as the remarks at the end of this section, should be consulted in this connection.

[152] M. WUNDER and V. THÜRINGER, *Z. anal. Chem.* **52**, 101, 660, 740 (1913).

[153] Strictly speaking, the specific precipitability of Pd^{++} ions from acid solutions by dimethylglyoxime holds only for nitric acid solutions. In hydrochloric acid solutions, gold salts are reduced quantitatively to the free metal by dimethylglyoxime. With reference to platinum salts, it can be pointed out that, in hydrochloric acid solutions, prolonged action of dimethylglyoxime gradually produces a green-blue precipitate, but the deposition is incomplete. If palladium also is present, this precipitation is more rapid (probably because of induction), and can be perceived through a greenish coloration of the Pd dimethylglyoximate. Probably in hydrochloric acid solution, dimethylglyoxime partially reduces the platinum to the divalent condition which, analogous to divalent palladium, forms an insoluble inner complex dimethylglyoxime salt. In this connection, see W. R. SCHÖLLER and A. R. POWELL, The Analysis of Minerals and Ores of the Rarer Elements, 2nd Ed., page 272. Edinburgh, 1940.

ions, but in other ways.   The addition of dimethylglyoxime and ammonia to solutions of these ions results in characteristic color changes that can be used for analytical purposes.   An ammoniacal copper solution gives a red-brown color with dimethylglyoxime, and a .violet shade if oxidizing agents are present.[154]   The chemical basis of these color reactions has not been elucidated.   Tschugaeff[155] was the first to observe the red color produced with ferrous salts.   It develops when a tartrated ferrous solution is treated with dimethylglyoxime plus ammonia or a water-soluble aromatic amine.   The compound responsible for this color reaction has not been isolated, but it has been assumed to be an addition compound of two molecules of ammonia (or amine) and an inner complex ferrous dimethylglyoximate, i.e., $Fe(DH)_2 \cdot 2NH_3$.   (Dimethylglyoxime is commonly abbreviated DH_2.   Hence DH represents the univalent and D the divalent acid radical of DH_2.)   It seems, however, that another constitution is more appropriate (see infra).[156]   The brown-violet color, observed by Tschugaeff (loc. cit.), produced by adding dimethylglyoxime to an ammoniacal cobalt solution, has been found by Feigl and Rubinstein[157] to be the result of the formation of bis-dimethylglyoxime-cobalto ions $[Co(DH_2)_2]^{++}$, along with soluble hydroxides of this ion.   A consideration of the action of the dioxime group toward Ni^{++}, Pd^{++}, Fe^{++}, Co^{++}, and probably also Cu^{++} ions, shows that this group sometimes acts as an inner complex former, i.e., both salt-forming and coordinative, and sometimes solely coordinative.   These multiple abilities, together with the maintenance of definite reaction conditions, have made it possible to develop a considerable number of specific and selective tests and methods of determination, based on the use of dimethylglyoxime and other α-dioximes.[158]

[154] S. G. CLARK and B. JONES, Analyst 54, 333 (1929); I. M. KOLTHOFF, J. Am. Chem. Soc. 52, 2222 (1930); L. C. HURD and J. S. CHAMBERS, Ind. Eng. Chem., Anal. Ed. 4, 236 (1932).

[155] L. TSCHUGAEFF, Z. anorg. allgem. Chem. 46, 144 (1905).

[156] The formation of Fe^{II} dimethylglyoximate from ferric salts after reduction with stannous chloride was used by FEIGL as a delicate test for tin.   [Chem. Ztg. 43, 261 (1919)].   The finding by G. CHARLOT [Bull. soc. chim. 57, 144 (1940)] is interesting from the analytical standpoint.   He observed that the red alkaline solution of Fe^{II} dimethylglyoximate, which is readily oxidized with loss of its color, can serve to detect oxidants that are active in basic media.

[157] F. FEIGL and H. RUBINSTEIN, Ann. 433, 183 (1923); compare also E. THILO and K. FRIEDRICH, Ber. 62, 2998 (1929).

[158] An excellent review of the analytical use of dioximes is given in the monograph by H. DIEHL, The Application of the Dioximes to Analytical Chemistry, G. F. Smith Chemical Co., Columbus, Ohio, 1940.   This booklet does not contain any reference to the: Detection of cobalt with dimethylglyoxime and ammonium sulfide, K. KRAUT [Z. angew. Chem. 19, 1793 (1906); F. FEIGL and L. v. TUTSTANOWSKA, Ber. 57, 762

The following somewhat surprising facts concerning the constitution of metal compounds of dimethylglyoxime merit attention.[158a] Yellow Pd dimethylglyoximate dissolves readily, and with a yellow color, in alkali hydroxide.[159] The addition of Ni^{++} ions to this yellow solution (or to the yellow solution in ammonia) yields no precipitate of red Ni-dimethylglyoxime. Consequently, when $Pd(DH)_2$ dissolves in basic media, the dimethylglyoxime is not set free, but remains linked with the palladium. Palladium dimethylglyoximate can be precipitated quantitatively from its yelllow solutions by acids, and the addition of barium hydroxide produces yellow crystalline $Ba[PdD_2]$. If the barium salt is isolated, and then digested with salts of Pd^{++}, Mn^{++}, and Pb^{++}, pure specimens of $Pd[PdD_2]$, $Mn[PdD_2]$, and $Pb[PdD_2]$, are obtained. It is remarkable that the palladium, manganese, and lead compounds are, respectively, brown, dark brown, and scarlet. The scarlet lead salt can also be obtained directly by digesting Pd dimethylglyoximate with a solution of basic lead acetate.

The solubility of $Pd(DH)_2$ in alkali hydroxides, and the formation of compounds in which dimethylglyoxime is bound both to palladium and to another metal atom, can be explained as follows. $Pd(DH)_2$ is a pseudo-acid, i.e., the intact NOH groups contained in the inner complex $Pd(DH)_2$, as shown by the coordination formula, are acidic in character. When salts of these NOH groups are produced by adding strong alkali, the soluble alkali salts retain the inner complex ring:
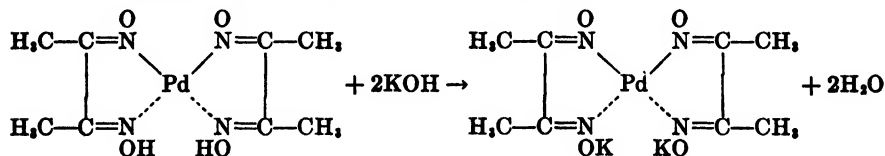
Written in the general form, this becomes:

$$Pd(DH)_2 + 2OH^- \rightarrow PdD_2^{--} + 2H_2O$$
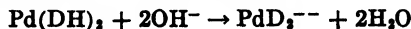
The compound $KH[PdD_2]$ has actually been isolated from the solution of $Pd(DH)_2$ in potassium hydroxide. Consequently, it is very probable that a dipotassium salt exists in the presence of excess potassium hydroxide.

(1924)]; Quantitative determination of nickel with oxalenediuramidoxime [F. FEIGL and A. CHRISTIANI-KRONWALD, Z. anal. Chem. **65**, 341 (1925)]; Quantitative nickel determination with oxalenediaminedioxime [R. CHATTERJEE, Chem. Abstracts **33**, 2841 (1939)]; Detection of palladium with nickel dimethylglyoxime [F. FEIGL, Chemistry & Industry **57**, 1161 (1938)].

[158a] F. FEIGL and H. A. SUTER, J. Chem. Soc. **151**, 378 (1948).

[159] R. A. COOPER, J. Chem. Met. Mining Soc. S. Africa **25**, 296 (1925).

The formation of the yellow barium salt and its metathesis with solutions of metal salts can be written:

$$K_2[PdD_2] + Ba(OH)_2 \rightarrow Ba[PdD_2] + 2KOH$$
$$Ba[PdD_2] + Me^{++} \rightarrow Me[PdD_2] + Ba^{++}$$
$$(Me = Pd^{++}, Mn^{++}, Pb^{++}, etc.)$$
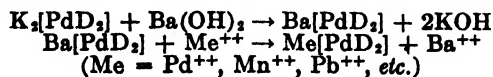
The fact that palladium dimethylglyoximate forms salts with alkali, alkaline earth, and heavy metals, is a nice proof for the correctness of its coordination chemical formulation as an inner complex salt, since the coordination formula stipulates the presence of free acidic NOH groups. In addition, it may be expected fundamentally that inner complex salts of organic compounds which contain two acidic groups may be soluble in alkali hydroxides, when only one of the acidic groups is salified. Indications of this are given by the behavior of salicylaldoxime and other o-oxyaldoximes as discussed on p. 200. The copper, nickel, and cobalt inner complex salts of salicylaldoxime contain NOH groups that are not salified; they dissolve in ammonia and alkali hydroxides. Therefore, it is quite likely, although no experimental evidence can be cited, that the mechanism by which the inner complex salts of salicylaldoxime (and other o-hydroxyaldoximes) dissolve in alkalies is analogous to that involved in the solution of Pd dimethylglyoximate in alkalies.[160]

The production of yellow, water-soluble $K_2[PdD_2]$ when Pd(DH)$_2$ dissolves in alkalies indicates strongly that the Tschugaeff color reaction (ferrous salt + dimethylglyoxime + ammonia) is due to the formation of an analogous compound. Formerly it was assumed that the product is an inner complex ferrous dimethylglyoximate with added ammonia molecules, Fe(DH)$_2$·2NH$_3$. Now it seems more likely that soluble (NH$_4$)$_2$[FeD$_2$] is formed, and that its anion [FeD$_2$]$^{--}$ is red. This interpretation is supported by the success of Thilo and Friedrich,[161] who prepared Li$_2$[NiD$_2$], which is not stable to water, by treating Ni dimethylglyoximate with lithium ethylate in absolute ethyl alcohol. Additional evidence of the behavior of dimethylglyoxime as a dibasic acid is given by the compound FeCoO$_{12}$H$_{19}$N$_6$O$_6$, isolated by Weeldenburg (see pp. 83, 274). This obviously should be formulated as a binuclear compound: D=Fe—DH . . . Co=D.

[160] The following remarkable fact is of interest here. Both the red nickel salt and the yellow palladium salt of dimethylglyoxime dissolve in chloroform. Although this solubility is low, both of these solutions are yellow. Ni dimethylglyoximate dissolves also in hot oleic acid, melted paraffine, naphthaline, etc., to form yellow solutions. It is well known that red mercuric iodide forms colorless solutions in acetone. These instances are cited here to direct attention to the fact that the color of a material in the solid state is not necessarily identical with the color of its solution in an organic liquid or melt.

[161] E. THILO and K. FRIEDRICH, Ber. 2998 (1929).

The ability of complexly bound dimethylglyoxime to form water-soluble alkali salts appears in two very sensitive and selective reactions for nickel and cobalt. The chemistry of these tests is quite interesting. Practical experience showed that the dimethylglyoxime precipitation of nickel is incomplete in the presence of large amounts of nitrate, pink solutions being formed. Since no peptizing action is likely, the author suspected that the nitrate was exercising an oxidizing effect. Actual trials demonstrated that many solid or soluble oxidants may dissolve nickel dimethylglyoximate suspended in alkali hydroxide or ammonia and produce a pink solution.[162] Accordingly, a red solution rather than a red precipitate results when the nickel plus dimethylglyoxime reaction is carried out in ammoniacal solution in the presence of oxidants. Neutralization of such red alkaline solutions produces a black-red material, which can be purified by redissolving it in alkali and again neutralizing. The analytical data, and the quantity of iodine liberated when the product is decomposed by acid in the presence of potassium iodide, indicate that the material is a compound of quadrivalent nickel as shown in (I). In view of the solubility in alkali of palladium dimethylglyoximate (see p. 276) it is quite probable that the solubility of (I) in sodium hydroxide or carbonate is due to the formation of a sodium compound of the structure (II). Accordingly, the latter is a compound possessing an inner complex anion, whose constitution is analogous to that of potassium palladium dimethylglyoximate.
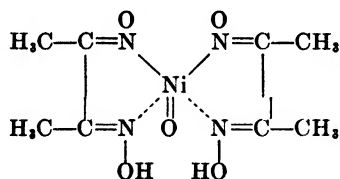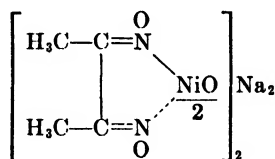
(I)   (II)

In the course of the study of the reaction between nickel ions and dimethylglyoxime in alkaline solution in the presence of oxidants, it was found that the color reaction resulting from the formation of soluble Ni^{IV} dimethylglyoximate is about 50 times as sensitive as the precipitation of the familiar red Ni^{II} dimethylglyoximate. Consequently, it seemed likely that the production of the water-soluble Ni^{IV} compound could be made the basis of a colorimetric method of determining nickel. This expectation was fulfilled within a short time when Rollet[163] described a procedure of this kind and, with slight modifications, it has been widely

[162] F. FEIGL, *Ber.* **57, 758** (1924).
[163] P. ROLLET, *Compt. rend.* **183, 212** (1926).

used for small amounts of nickel.   Haim and Tarrant's[164] recommendation to use iodine in ammoniacal solution as oxidant has been substantiated by the writer's own experience.

Special attention should be given here to the finding of Rollet (*loc. cit.*) that the red Ni^{IV} dimethylglyoximate compound can also be produced from solutions that contain CN$^-$ ions.   Consequently, it is resistant to potassium cyanide.   If it is recalled that Ni^{II} dimethylglyoximate and all other known inner complex nickel salts are soluble in this reagent, with production of K$_2$[Ni(CN)$_4$], the exceptional stability of quadrivalent nickel in the inner complex linkage with dimethylglyoxime is amply demonstrated.

A sensitive and selective cobalt reaction, that likewise may be associated with the acidic nature of complex-bound dimethylglyoxime, was discovered by Kraut.[165]   The basis of this test is the fact that the addition of alkali sulfide to ammoniacal cobalt solutions containing dimethylglyoxime does not result in a precipitate of CoS; a red-violet color develops instead.   When the colored solution is acidified, an insoluble product is obtained, which can be purified by solution in alkali and reprecipitation with acid.[166]   Analysis indicates that the product has the empirical formula (III) or the dimeric structure (IV):

$$CoS \cdot DH_2 \cdot H_2O \cdot NH_3$$

(III)

(IV)
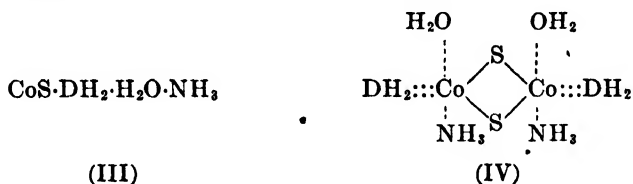
Probably, the solubility in alkali of (III) or (IV) is likewise due to the ability of complexly bound dimethylglyoxime to combine with alkali salts.

It seems now to have been established that dimethylglyoxime (and, in all likelihood, other α-dioximes) can function in three different ways:

(1) As the neutral portion through coordination of the NOH groups by their nitrogen atoms;

(2) As monobasic acids, by forming a salt of one NOH group, and coordinative linking of the other NOH group;

(3) As dibasic acids, by salifying both NOH groups, either with or without coordination of their nitrogen atoms.

[164] G. HAIM and B. TARRANT, *Ind. Eng. Chem., Anal. Ed.* **18**, 51 (1946).   This contains a bibliography of the colorimetric determination of nickel through the production of Ni^{IV} dimethylglyoximate.

[165] K. KRAUT, *Z. angew. Chem.* **19**, 1793 (1906).

[166] F. FEIGL and L. v. TUSTANOWSKA, *Ber.* **57**, 762 (1924).

These diverse activities of α-dioximes, or of their —C(:NOH)—C(:NOH) groups, constitute the basis of the chemistry of all the known applications of these compounds.

SELECTIVE ACTIONS OF ORGANIC NITRO COMPOUNDS TOWARD ALKALI METALS

The highest electroaffinities among metals are possessed by the alkali metals (Li, Na, K, Rb, Cs). They form the most stable ions and, consequently, there are exceedingly few examples of the precipitation of insoluble inorganic alkali salts from pure aqueous solutions. Even these precipitates, for the most part, are complex double salts. Hence, it is rather remarkable that certain organic nitro compounds are capable of forming relatively difficultly soluble binary salts with potassium, rubidium, and cesium, the corresponding lithium and sodium salts being quite soluble in water.[167] Since the atomic volumes increase markedly from lithium to cesium, their salts with organic nitro compounds display clearly a relationship between the solubility of the salts in water and the atomic volumes of the respective metals.

The following nitro compounds produce crystalline salts with potassium (also Rb and Cs) from neutral or alkaline solution. The solubility of the salts is relatively low, and some of these products have even been recommended for the quantitative determination of potassium.

Picric acid[168] o- and p-Nitrophenol[169] 2,4- and 2,6-Dinitrophenol[169]

Trinitro-m-cresol[169] Trinitroresorcinol[169] 6-Chloro-5-Nitrotoluene-3-Sulfonic acid[170]
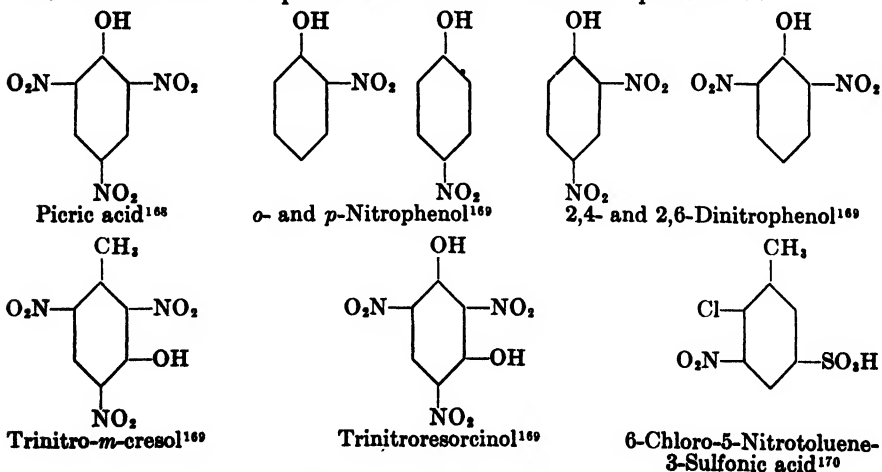
[167] An analogous effect of NO₂ groups has been encountered among inorganic compounds also. Water-insoluble alkali cobaltinitrites are formed by the union of [Co(NO₂)₆]⁻⁻⁻ ions with K⁺, Rb⁺, and Cs⁺ ions, whereas Li⁺ and Na⁺ ions are not precipitated.

[168] J. LIEBIG, Ann. Physik 13, 201 (1828).

[169] L. ROSENTHALER, Mikrochemie 2, 29 (1924).

[170] H. DAVIES and W. DAVIES, J. Chem. Soc. 123, 2976 (1923).
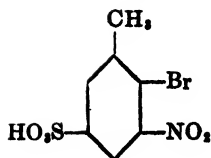
2-Bromo-3-nitro-
toluene-5-sulfonic
acid[171]
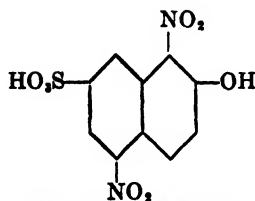
1,5-Dinitro-2-naphthol-
7-sulfonic acid[172]
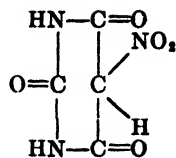
5-Nitrobar-
bituric acid[173]
(dilituric acid)
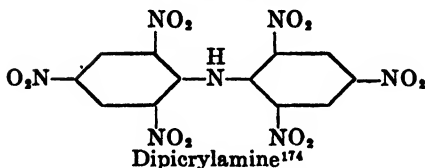
Dipicrylamine[174]

A study of the constitution of these nitro compounds which act as precipitants for potassium in neutral or alkaline solution, reveals that only the sulfonic acids present no problem regarding the mechanism of the reaction; in them the potassium may replace the hydrogen of the SO_3H group. In the other cases, the phenolic OH groups or the NH groups at first sight seem to be the potassium-binding groups. However, these groups, when present in NO_2-free compounds, display no precipitating action toward potassium ions. Since all the OH- and NH-bearing compounds listed here offer the possibility of a transformation (enolization) of NO_2 groups into isonitro $=NO_2H$ groups, it appears most probable that the formation of the potassium salt does not directly involve an OH or NH group, and the active group, accordingly, is the aci- or isonitro group. This assumption is supported by the fact that nitrophenols can be employed as indicators in neutralization titrations.[175] The color changes which they display when certain pH values are passed are ascribed to a rearrangement producing quinoidal compounds. For example, p-nitrophenol is assumed to present the following equilibria:

Phenolic aci-form
(colorless)

Isonitro-aci-form
(yellow)
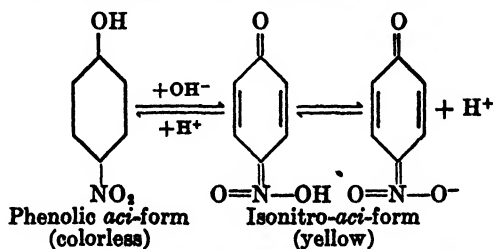
[171] V. H. DERMER and O. C. DERMER, J. Am. Chem. Soc. 60, 1 (1938).

[172] E. P. VOLOCHNEVA, J. Applied Chem. (U.S.S.R.) 11, 369 (1938).

[173] H. FRIEDHOLM, Z. anal. Chem. 104, 400 (1936).

[174] N. S. POLUEKTOFF, Mikrochemie 14, 265 (1934).

[175] Compare L. MICHAELIS and A. GYEMANT, Biochem. Z. 109, 165 (1920).

Hantzsch[176] originated the concept that aliphatic and aromatic nitro compounds can undergo rearrangement into tautomeric *aci*-nitro forms. This postulate provides a satisfactory explanation of the many observations concerning the color changes that accompany the solution of organic mono- and polynitro compounds in aqueous or alcoholic solutions of sodium hydroxide. The nitro compounds, most of which are yellow, produce characteristic red, violet, or blue solutions in alkali. Sodium salts of *aci*-nitro compounds are formed.[177]

The behavior of dipicrylamine (hexanitrodiphenylamine) toward OH⁻ and K⁺ ions also harmonizes with this activity of nitro groups in an *aci*-form. It is the best organic precipitant for potassium discovered up to now. The yellow solid (I) is practically insoluble in water. On treatment with aqueous solutions of NaOH or Na₂CO₃, it forms orange-red solutions, from which the yellow dipicrylamine is again precipitated by mineral acids. The solution and reprecipitation can be represented as reversible conversions of nitro (*baso-*) and isonitro (*aci-*) forms of dipicrylamine:

(I)
Dipicrylamine
(*baso*-form)

(II)
Dipicrylamine (*aci*-form)

(III)
Potassium dipicrylaminate
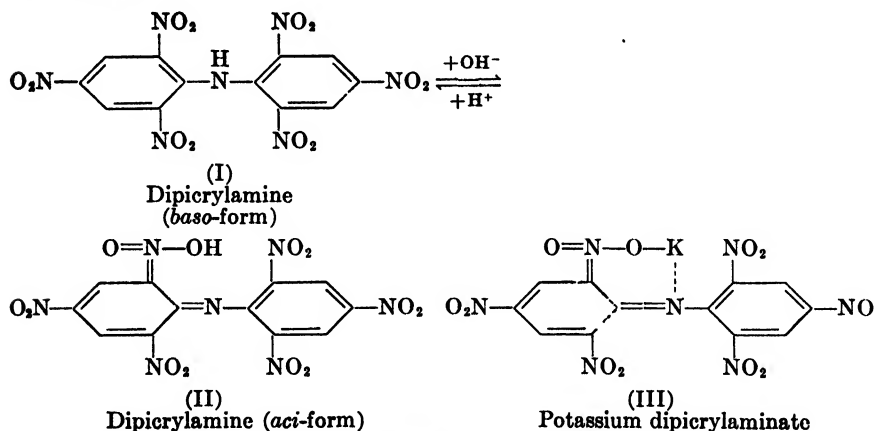
[176] A. HANTZSCH and J. LISTER, *Ber.* **43**, 1686 (1910).

[177] An excellent review of the literature and the newer findings concerning color reactions accompanying the solution in alkali of phenylhydrazones containing NO₂ groups is given by C. NEUBERG and E. STRAUSS, *Arch. Biochem.* **7**, 211 (1945). Compare C. L. JACKSON and R. B. EARLE, *Am. Chem. J.* **29**, 89 (1903) and also J. MEISENHEIMER, *Ann.* **323**, 205 (1902) with regard to the solubility of polynitro compounds in basic solutions. Neuberg and Strauss (*loc. cit.*) demonstrated that dicarbonyl compounds can be determined colorimetrically by precipitating their 2,4-dinitrophenylhydrazones from acid solutions and then dissolving the precipitate in alcoholic sodium hydroxide. Minute amounts (1-2γ/ml.) of the dicarbonyl compound in the form of its hydrazone can be determined in this way. Another interesting application of the production of colored alkali salts of *aci*-nitro compounds is due to M. S. SCHECHTER, S. B. SOLOWAY, R. A. HAYES and H. L. HALLER, *Ind. Eng. Chem., Anal. Ed.* **17**, 704

A comparison of the *baso*-form (I) and the *aci*-form (II) of dipicryl-amine shows that the latter contains not only the acidic isonitro group but also a continuous system of conjugated double bonds. This doubt-less is responsible for the great difference in color and solubility of the two tautomeric forms of dipicrylamine. The water-insoluble *baso*-form is by no means a general reagent for potassium; it reacts only with solutions of KOH or K_2CO_3. In these, the OH^- ions bring about rearrangement into the *aci*-form. The formation of the potassium salt then follows, as is revealed by the change from yellow to red. On the other hand, a solution of the sodium salt reacts with all soluble potassium salts to produce a red precipitate of potassium dipicrylaminate. The latter, in contrast to solutions of the sodium salt, is resistant to dilute mineral acids. The potassium salt of dipicrylamine may possibly be an inner complex salt as represented by (III). Arguments in favor of this formu-lation of the salt are its slight solubility in water, its relative stability (after precipitation) against mineral acids, and its solubility in organic nitro compounds (nitrobenzene, nitromethane, *etc.*).

Poluektoff[178] introduced dipicrylamine into analytical practice as a reagent for potassium. The selectivity of the precipitating action is noteworthy. Only cesium, rubidium, and thallous ions likewise form dipicrylaminates that are no more than slightly soluble. The low solu-bility of the ammonium salt presents no serious difficulty because ammonium salts can be removed by ignition. The reagent solution consists of the sodium salt, whose solubility in water, however, is not great enough to do away entirely with the danger of the reagent being salted out in concentrated solutions of sodium salts. Consequently, in the presence of sodium, the limiting proportion for the detection of potassium, as a spot test, is only 1:100, and the identification limit is only 25γ potassium. When potassium is present alone, the identifica-tion limit is 3γ potassium.

Dipicrylamine obviously cannot compete with the majority of the organic reagents for heavy metals on the basis of attainable identification and concentration limits. Nevertheless, it has distinct advantages. For instance, it is the first precipitant for potassium that can also be used in

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(1945). They subjected the degradation products of DDT [l-trichloro-2,2-bis(*p*-chloro-phenyl) ethane] and its related compounds to extensive nitration. The resulting tetranitro product was converted into its alkali salt and measured colorimetrically. These examples are cited here because they support the viewpoint adopted in this book, namely, that organic nitro compounds, when used for analytical purposes, react in the *aci*-form. Compare the remarks on p. 255 (1-nitro-2-naphthol) and on p. 285 (nitroquinoline).

[178] N. S. Poluektoff, *Mikrochemie* **14**, 265 (1934).

spot testing.[179] There is every reason to expect the future discovery of other and perhaps better organic reagents for potassium among those nitro compounds in which a shift of hydrogen atoms results in the production of acidic isonitro groups. The way for this advance has been paved by the experience gained with dipicrylamine.

The Palladium-Specific Action of 6-Nitroquinoline

Ogburn and Riesmeyer[180] found that a flocculent yellow precipitate appears if a solution of palladous chloride is warmed with a saturated aqueous solution of 6-nitroquinoline (I). After it has once been formed, the precipitate is resistant to concentrated hydrochloric acid. They analyzed the product, dried at 105°C., and assumed from the data that the empirical formula is $Pd(C_9H_6N \cdot NO_2)_2$. Accordingly, the precipitate would be the result of a combination of nitroquinoline and palladium, without replacement of hydrogen atoms of the organic reagent. Within the platinum group, the precipitation is strictly specific, since the other metals (Ir, Rh, Ru, Os, Pt) do not react. Ogburn and Riesmeyer proved that this Pd-nitroquinoline precipitate is suitable for the gravimetric determination of palladium. Nothing has been reported concerning the behavior of metals outside the platinum group, nor are figures available on the precipitation sensitivity of the palladium reaction.

The chemistry of the precipitation of palladium by 6-nitroquinoline has not yet been elucidated. Ogburn and Riesmeyer assigned structural formula (II) to the precipitate. Hence, the reaction would be:
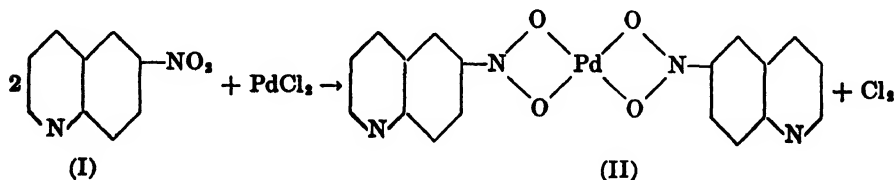
This implausible equation represents a reaction in which Pd^{II} is oxidized to Pd^{IV}, and Cl^- to $Cl°$. Should it be valid, other aromatic nitro compounds, including those without basic character, could be expected to react analogously, but at present there is no corroborating evidence. Likewise, no analogously constructed salts of nitro compounds with other metals are known. All previous experience has shown that salt-formation with an NO_2 group occurs only when this group can enolize to form

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[179] For literature on the analytical applications of dipicrylamine see F. J. WELCHER, op. cit., Vol. IV, New York 1948.

[180] S. C. OGBURN and A. H. RIESMEYER, J. Am. Chem. Soc. 50, 3018 (1929).

an isonitro or acinitro group, $=N—OH$. Consequently, it appears necessary to assume that 6-nitroquinoline (I) functions in the palladium reaction in the tautomeric form of an isonitroquinoline, whose structure may possibly be (Ia).[181] The following equation would then be in order:

(I)   (I(a))

$$(I(a)) + \tfrac{1}{2}PdCl_2 \rightarrow \qquad\qquad + HCl$$
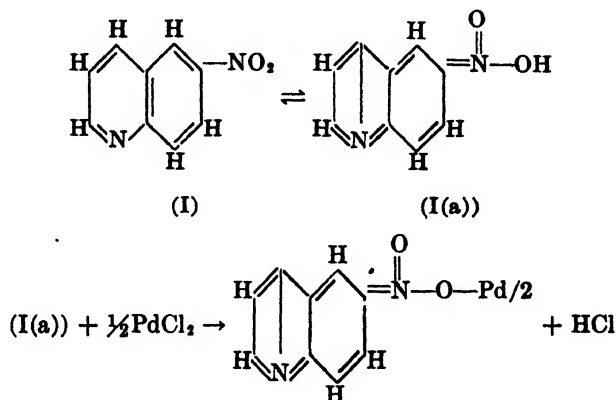
The palladium compound produced by this reaction would be a normal rather than a complex salt. It contains two hydrogen atoms less than the compound assumed to be formed by Ogburn and Riesmeyer. This slight difference in composition cannot be ascertained by analysis.

A proof of constitution, as well as a test of the assumption that nitroquinoline reacts in a tautomeric form, will have to follow other lines. Illuminating information could be obtained from a study of the behavior of the three isomeric methylated 6-nitroquinolines in which the methyl group is attached to the pyridine ring. According to the preceding structural formula and equation, either the 2- or the 3-methyl-6-nitroquinoline could react with $PdCl_2$, but not the 4-methyl-6-nitroquinoline, because the tautomerism demanded by (Ia) is not possible in this latter isomer. Further light would be shed by a study of the action of methyl iodide on the palladium salt. The metal could be replaced by the methyl

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[181] This postulation of a tautomeric form of quinoline is not made *ad hoc*. The assumption of the existence of isomeric forms of quinoline and pyridine makes certain reactions of these bases plausible. Compare V. GRIGNARD, Precis de chimie organique, pp. 721, 735. Paris 1937. The formula (Ia), accepted here tentatively, appears at first to be less satisfactory. The chief objection is the binding of the nitrogen atom to a *para* doubly bound carbon atom. However, no other formulation is possible, if the nitrogen is assumed to be quinquevalent in the NO_2 and NO_2H groups, and the formation of a radical with trivalent carbon is ruled out. Perhaps a more appropriate explanation can be secured from the standpoint of resonance.

group, with concurrent formation of PdI_2. If a nitromethyl ether should be produced by this reaction, the aci-form would be substantiated directly. If the more probable reaction occurs, namely the reversal of the rearrangement, products containing a methyl group in the pyridine ring of 6-nitroquinoline would result. These derivatives could give information concerning which position of the pyridine ring delivers a hydrogen atom when the aci-form is produced.

There is still another possibility for explaining the singular behavior of 6-nitroquinoline toward palladium salts. Meisenheimer[182] proved that the α-unsaturated (aromatic) nitro compounds can undergo a rearrangement into the isomeric oximes. For instance, the isomeric o-quinone oxime is obtained from 2-nitronaphthalene. 6-Nitroquinoline is likewise an α-unsaturated aromatic nitro compound and structurally it is entirely comparable to 2-nitronaphthalene. If the oxime rearrangement (I), which was demonstrated to take place by Meisenheimer, is compared with an analogous transformation (II) of 6-nitroquinoline, the following results become evident:

(I)   (II)
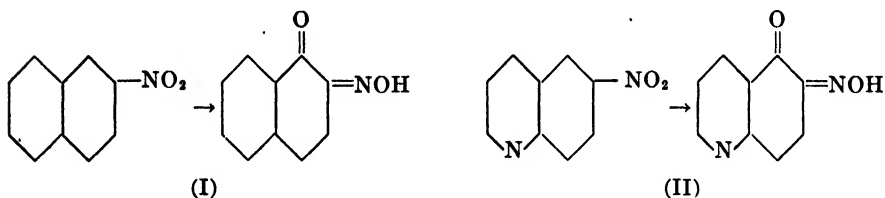
The oxime form of 2-nitronaphthalene is simply the oxime form of 2-nitroso-1-naphthol, and the latter (see p. 253) is known to form an inner complex acid-stable palladium salt. An oxime rearrangement of 6-nitroquinoline according to (II) would consequently lead to the development of an atom grouping which assuredly would be capable of forming a salt with palladium. Hence, the assumption that 6-nitroquinoline reacts in an isomeric oxime form with palladium cannot be ruled out. In this connection, however, it must be noted that the Meisenheimer rearrangement only occurs when nitro compounds are warmed with sodium methylate, and the transformation is irreversible. This signifies that there is no tautomerism between the nitro and the oxime forms, but rather an isomerism that is independent of pH. The palladium reaction takes place directly with the nitro compound with no alkalization. Hence, the involvement of a tautomeric equilibrium is indicated. It is constantly disturbed by the removal of the oxime form and thus a quantitative precipitation of palladium ions becomes possible.

[182] J. MEISENHEIMER, *Ann.* **323**, 205 (1902); **355**, 249 (1907); *Ber.* **36**, 4164 (1903).

Pd^{++} ions react immediately with 6-nitroquinoline in neutral solution; the Pd-salt, once it has been formed, is quite acid-resistant; the salt is light-colored, whereas an inner complex salt of an o-quinoneoxime would be expected to have a more intense color. The foregoing observations lead to the conclusion that another type of rearrangement may well be considered. If it is assumed, that the slightly water-soluble 6-nitroquinoline in its aqueous solutions is in tautomeric equilibrium with its o-hydroxynitro form, which forms an acid-stable salt with Pd^{++} ions, the following scheme emerges:
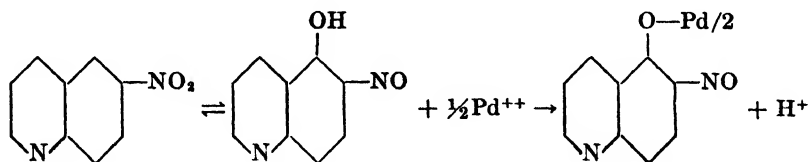
If the foregoing assumption is valid, the Pd-salt would not be viewed as the salt of an oxime or of an *aci*-nitro form, but as a phenolate. A tautomerism of aromatic nitro compounds of the preceding type has not been known hitherto. The specificity of 6-nitroquinoline toward Pd salts may, however, be related to such a condition. In that case, an analogous ability to form salts with Pd^{++} ions can be expected among other aromatic nitro compounds.

The interesting palladium reaction, whose analytical value is beyond question, obviously merits further study in order to clear up its chemical basis and to clarify the constitution of the resulting salt. If the formulation suggested by Ogburn and Riesmeyer should unexpectedly prove to be correct, the reaction would be of an unique type, and for this reason alone should be given every consideration. If one of the possibilities suggested by the author should prove to be acceptable, then, for the first time, through the production of a salt, there would be proof of the tautomerism of quinoline, or of the pyridine ring it contains. Acceptance of the other postulate would show that an oxime rearrangement of aromatic nitro compounds is possible by a means other than that discovered by Meisenheimer. Both of these prospects have considerable interest. This example illustrates the important fact that considerations of selective actions of groups may have significance beyond the purely analytical objective; they can render valuable service in solving problems concerning the isomerism and tautomerism of organic compounds.

The analytical behavior of other mono- and polynitroquinolines should be studied. The findings would, of course, supplement the present knowledge of group actions in organic reagents. They also

might lead to applications of these compounds, which, in general, are more readily available than 6-nitroquinoline.

ACIDIC INORGANIC GROUPS IN ORGANIC COMPOUNDS

Di- and tribasic inorganic acids may be combined with organic radicals in ways that are fundamentally different. Sometimes they form ester acids, in other instances the union is between a carbon atom of the organic radical and the acid-forming non-metallic central atom. The linking of organic residues to inorganic acid groups frequently results in far-reaching alterations in the character of the mineral acid. This effect manifests itself, for instance, in changed solubility relations· of the respective acids and their salts. Occasionally, this modification of characteristics leads to selective actions that have analytical applications.

In actual practice, the acidic SO_3H group is the easiest to introduce into organic radicals. A solubility-promoting effect results almost invariably, and good use can be made of this (see p. 257). The few known examples of difficultly soluble salts of substituted aromatic sulfonic acids have no analytical significance.[182a] Sulfinic and seleninic acids exert selective actions by forming insoluble salts. The SO_2H group, in such cases, however, does not react analogously to the SO_3H group, but functions in a tautomeric form (see p. 290). Organic derivatives of arsenic and phosphoric acids provide selective precipitation reactions that can be utilized for both qualitative and quantitative purposes.

This section will also include a discussion of the analytical behavior of inorganic and organic derivatives of hydrogen peroxide, which itself may be regarded as a weak acid. All of these compounds contain the —O—OH group, which displays interesting catalytic effects that can be used to detect this group.

Not a great deal is known about the analytical behavior of organic derivatives of inorganic oxyacids. This is due in part to the relative difficulty of obtaining most of these compounds. Special interest would attach to materials possessing inorganic acidic groups in coordinative positions relative to atoms that have auxiliary valence capabilities. Such compounds will probably display selective actions through the production of inner complex salts.

[182a] An interesting exception is 2-hydroxy-5-methylazobenzene-4-sulfonic acid. V. J. KUZNETSOV [*Chem. Abstracts* **35**, 2092 (1941)] found that this acid is a selective precipitant for zirconium and hafnium. However, it is very unlikely that the SO_3H group is salified, but rather the action of the reagent is probably due to a phenolic metal binding and formation of an adsorption compound (compare Chapter X) with hydrolysis products of zirconium and hafnium salts.

The Selective Activity of the SO_2H *and* SeO_2H *Groups*[183]

Water-soluble benzenesulfinic acid, $C_6H_5SO_2H$, or its alkali salts react with ferric salts, even in the presence of mineral acids, to produce a precipitate of slightly soluble orange-yellow ferric benzenesulfinate, $Fe(C_6H_5SO_2)_3$.[184] The low solubility product of this salt is evidenced by the fact that the precipitation occurs even in solutions containing phosphate or fluoride ions, where, because of the formation of complex ions, there is only a very low concentration of Fe^{+++} ion. Correspondingly, very dilute ferric solutions, that scarcely give a noticeable pink with thiocyanates, produce a distinct turbidity with benzenesulfinic acid. Several quadrivalent metal ions likewise react in acid solution with benzenesulfinic acid, and produce precipitates whose composition corresponds to the anticipated formula. Examples are cerium[IV], thorium, and uranium[IV]. Titanium[IV] and tin[IV], as well as zirconium, are precipitated quantitatively; however, these precipitates do not conform to the composition demanded by the formula, but consist chiefly to $TiO_2 \cdot aq$, $SnO_2 \cdot aq$, or the basic zirconium salt. Consequently, benzenesulfinic acid can be regarded as a group reagent for quandrivalent metals. Their pure sulfinates have a simple structure with the general formula $Me(C_6H_5SO_2)_4$. It is worthy of note that cerium, which normally is trivalent, and uranium, that usually is hexavalent, produce stable benzenesulfinates at the quadrivalent level. Ordinarily, the salts corresponding to these anomalous valencies are easily reduced or oxidized. Since, the SO_2H group is easily converted into the SO_3H group by oxidizing agents, and cerium[IV] salts are strong oxidizing agents, the formation and stability of $Ce(C_6H_5SO_2)_4$ is particularly remarkable, because abnormal valencies ordinarily are stable only in the form of complex salts.

Other sulfinic acids, and also seleninic acids, react like benzenesulfinic acid toward these metal ions. Consequently, sulfinic and seleninic acids exhibit a remarkable selectivity, since they form precipitates in acid solution with only a few metal ions.

A comparison of the reactivity of benzenesulfinic acid (I), benzylsulfinic acid (II), and cyclohexylsulfinic acid (III), as well as of the three analogous seleninic acids, has shown that only benzenesulfinic acid or benzeneseleninic acid form slightly soluble precipitates with ferric and quadrivalent metal ions.

[183] Studies with V. Anger, Dissertation, Vienna 1936; compare F. Feigl, *Oesterr. Chem. Ztg.* **40**, 535 (1937).

[184] J. Thomas, *J. Chem. Soc.* **95**, 343 (1909).
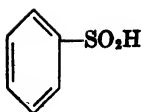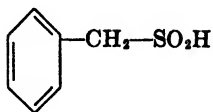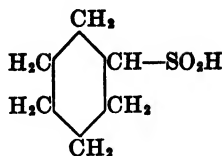
| (I) | (II) | (III) |

This leads to the conclusion that a direct attachment of the SO_2H or SeO_2H group to an aromatic ring determines the specific action. It thus seems obvious to assume that the phenyl group through its system of conjugated double bonds is coordinated on the metal atom in the insoluble benzenesulfinates.

If the empirical formulas are used as the sole criterion, sulfinic acids, RSO_2H, differ from sulfonic acids, RSO_3H, simply by one oxygen atom. Consequently, the fact that only the sulfinic acids form acid-resistant metal salts is striking, and this in itself indicates that the metal salts of these two classes of acids are constituted differently. The divergent behavior toward organic solvents shows that the acids themselves also do not have analogous constitutions. For instance, aromatic sulfinic acids are soluble in benzene and ether, and thus show a marked organic character that is in contrast to aromatic sulfonic acids, which do not dissolve in these liquids. The difference between sulfonic and sulfinic acids (and their salts) is obviously due to the fact that the —SO_3H and —SO_2H groups bound to an aromatic residue do not have the analogous constitutions: $(SO_2)\cdot OH$ and $(SO)\cdot OH$, respectively. The sulfinic acids can be viewed as organic derivatives of sulfurous acid. In them, there is probably a tautomerism of the SO_2H group:

| (I) | (II) |
| (Sulfin form) | (Sulfon form) |
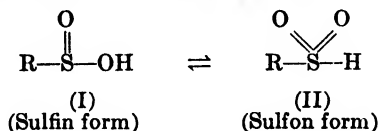
whose equilibrium even in water solution lies far in the direction of the sulfon form (II).[185] Accordingly, ferric and ceric benzenesulfinates are written here as inner complex salts of the sulfon form with the coordination formulas:

[185] This assumption is strengthened further by the fact that several reactions of sulfinic acids are known which are possible only as reactions of a sulfon form. In this connection compare W. J. HICKINGBOTTOM, Reactions of Organic Compounds, p. 400. London, 1940,

These methods of representation also satisfactorily account for the stability of the metals at abnormal valences. This stability is conferred here by the sexivalence of the sulfur atom and by the auxiliary valence linking. Analogous formulas may be valid for other slightly soluble metal sulfinates.

The seleninic acids behave differently. In contrast to the sulfinic acids, they react in acid solution also with molybdates and tungstates to produce white precipitates. The reactivity toward molybdates and tungstates is shown by all seleninic acids, no matter whether the radical attached to the SeO_2H group is aliphatic or aromatic. However, the precipitates are not molybdenum or tungsten salts; they are complicated molecular compounds, possibly of the heteropolyacid type.

The author and A. Lenzer have found (unpublished studies) that benzenesulfinic acid can be used for the quantitative determination and also the separation of iron, thorium, and uranium from other metals. They can be finally weighed as the benzenesulfinate.

Studies by the author, assisted by F. Hecht and F. Korkisch,[186] showed that the precipitation of thorium by p-iodobenzenesulfinic acid provides an excellent means of determining this metal by a microgravimetric procedure. Krishna and Singh,[187] from trials with twelve different aromatic sulfinic acids, including some containing substituents, showed that it is possible to determine these acids quantitatively by precipitation with excess ferric chloride, and back-titration of the unused iron. They also determined iron quantitatively by titrating the ferric solution with 1% aqueous solution of benzenesulfinic acid, employing potassium thiocyanate as external indicator.

The Zirconium-Binding Group $\quad$ —As$\diagup\!\!\!=\!\!\!O$ with OH groups

$$\text{The Zirconium-Binding Group} \quad -\text{As} \underset{\diagdown OH}{\overset{\diagup OH}{=}} O$$

Arsenic acid precipitates white, amorphorous tertiary zirconium arsenate or $Zr(HAsO_4)_2$ from nitric or hydrochloric acid solutions of zirconium salts. This action of arsenic acid is retained in its monoalkylated derivatives (compare Chapter IX). Rice, Fogg and James[188] were the first to show this with the colorless phenylarsonic acid, $C_6H_5AsO(OH)_2$. Consequently, this acid may be employed as precipitant in the gravimetric determination of zirconium.

[186] Cited in F. HECHT and J. DONAU, Anorganische Mikrogewichtsanalyse, p. 215. Vienna, 1940.

[187] S. KRISHNA and H. SINGH, *J. Am. Chem. Soc.* **50**, 792 (1928); Compare also I. S. DUBSKY and co-workers, *Chem. Abstracts* **31**, 5712 (1937).

[188] A. RICE, H. FOGG and C. JAMES, *J. Am. Chem. Soc.* **48**, 895 (1926).

A study of the derivatives of phenylarsonic acid[189] showed that the precipitating action of the —AsO(OH)$_2$ group toward zirconium salts is conserved after the introduction of various substituents into the phenyl group. Table IX summarizes the activity and attainable limits of detection shown by the arsonic acids that were tested in saturated aqueous solution against 2 ml. of an acid zirconium chloride solution. It appears that there is no dependence of the reaction sensitivity on the molecular weight and the number of atoms in the precipitant. Likewise, the effect and position in the molecule of groups (NO$_2$, Cl, *etc.*) that raise the solubility of the arsonic acids, are also reflected in a greater solubility of the corresponding zirconium salts.

The zirconium precipitates obtained with the arsonic acids included in the table are white or yellowish. The introduction of the color-conferring azo group results in derivatives of phenylarsonic acid that exhibit a very desirable improvement in their analytical effectiveness.[190] Thus the two azoarsonic acids:

$$(CH_3)_2N—C_6H_4—N=N—C_6H_4—AsO(OH)_2,$$
$$H_2N—C_6H_4—N=N—C_6H_4—AsO(OH)_2,$$
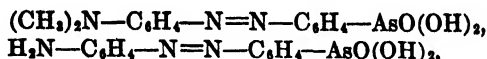
which are soluble in mineral acids by reason of their basic groups, give, in hydrochloric acid solution, colored amorphous precipitates even with slight amounts of zirconium. Since the color of the zirconium salt of an azoarsonic acid differs from that of the precipitant, it is possible, under definite experimental conditions, to detect successfully, by spot reactions, even small quantities of zirconium in the presence of large amounts of other metals. The most suitable material of this class is the yellow *p*-dimethylaminoazophenylarsonic acid, the first reagent to be used for this purpose.[191] Depending on the concentration conditions, this acid forms brown zirconium or zirconyl compounds of the composition:
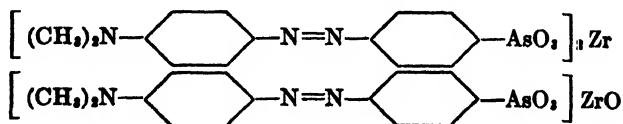
These compounds, after isolation, can be decomposed with ammonia. The yellow solution obtained after removal of the Zr(OH)$_4$ by filtration, may be used for the colorimetric determination of zirconium.[192]

[189] F. FEIGL and H. KAPULITZAS, unpublished studies; compare also H. KAPULITZAS, Dissertation, Vienna, 1930.
[190] F. FEIGL, P. KRUMHOLZ and E. RAJMANN, *Mikrochemie* 9, 395 (1931).
[191] F. FEIGL, Spot Tests, p. 155.
[192] W. G. HAYES and E. H. JONES, *Ind. Eng. Chem., Anal. Ed.* 13, 603 (1941).

TABLE IX

Name	Formula		Number of atoms. Molecular weight	Limit of identification mg. zirconium
Arsanilic acid.............	H_2N⟨benzene⟩AsO_3H_2		19 217.03	0.06
Acetarsanilic acid........	CH_3COHN⟨benzene⟩AsO_3H_2		24 257.02	0.016
Nitroarsanilic acid.......	H_2N⟨benzene⟩AsO_3H_2, O_2N		21 262.03	0.024
3-Chloroarsanilic acid.....	Cl, H_2N⟨benzene⟩AsO_3H_2		19 251.47	0.024
Dichloroarsanilic acid.....	Cl, H_2N⟨benzene⟩AsO_3H_2, Cl		19 285.92	0.024
Phenylglycinearsonic acid.	CO_2H, $H_2C \cdot HN$⟨benzene⟩AsO_3H_2		25 275.04	0.024
3-Nitro-4-hydroxyphenyl-arsonic acid.	O_2N, HO⟨benzene⟩AsO_3H_2		20 263.01	0.016
3,5-Dinitro-4-hydroxy-phenylarsonic acid.	O_2N, HO⟨benzene⟩AsO_3H_2, O_2N		22 308.00	0.024
p-Tolylarsonic acid........	H_3C⟨benzene⟩AsO_3H_2		20 216.03	0.024
m-Benzarsonic acid........	HO_2C⟨benzene⟩AsO_3H_2		20 246.01	0.016
Salicylarsonic acid........	HO_2C, HO⟨benzene⟩AsO_3H_2		21 262.01	0.016
Biphenylarsonic acid......	⟨benzene⟩-⟨benzene⟩AsO_3H_2		27 278.04	0.032
Methyl-4-hydroxyphenyl arsonic acid.	H_3C, HO⟨benzene⟩AsO_3H_2		21 232.03	0.024

The organic derivatives of arsenic acid are more sensitive precipitants for zirconium than the parent acid.   With them, the precipitation can be accomplished even in 1 N sulfuric acid solution, where, because of the formation of complex zirconiumsulfuric acids, the concentration of the zirconium ion is so diminished that several other tests for zirconium fail.

Craig and Chandlee[193] tested phenylarsonic acid and numerous substituted phenylarsonic acids, with respect to their behavior toward ferric salts.   They found that white ferric compounds are precipitated from slightly acid solutions.   This precipitability is in accord with the resistance of ferric arsenate to acetic acid, and also to quite dilute mineral acids.   The best precipitant is p-butylphenylarsonic acid.   Iron is quantitatively precipitated by it from 0.4 N hydrochloric acid and can thus be determined.

The behavior of the various arsonic acids toward ferric and zirconium solutions shows distinctly the relation of a selective precipitating action to acidity.   Even in the presence of ferric salts, zirconium, can be precipitated quantitatively from strongly acid solutions, without coprecipitation of iron.   The arsonic acids exhibit the precipitating action of the arsenic acids but in increased measure or, more correctly, at lower pH values.   Accordingly, bismuth, whose arsenate is not soluble in dilute mineral acids, can be precipitated from even strong acid solutions by phenylarsonic acid.   It would be logical, on this basis, to attempt a separation of bismuth and lead from mineral acid and acetic acid solutions.   Experiments along this line, including trials with various arsonic acids, would be of interest.

The Selective Action of Bis-p-Chlorophenylphosphoric Acid[194]

Bis-p-chlorophenylphosphoric acid (I) is a chlorodiphenyl ester of phosphoric acid.   Although practically insoluble in water, it dissolves readily in alcohol.   Its alkali salts form stable aqueous solutions, which act as quantitative precipitants when added to quite a few neutral salt solutions.   The chlorophenylphosphates of Ca, Sr, Ba, Mg, Fe^{II}, Co, Ni, Cu, and Cd are crystalline; the Fe^{III}, Al, Cr, Pb, and Sn^{IV} salts are amorphous.   Only colored metal ions produce colored chlorophenylphosphates.   Perhaps it is more than coincidence that all the crystalline salts are soluble in 1% hydrochloric acid, whereas the amorphous salts are decomposed only at higher concentrations of acid.

[193] K. A. CRAIG and G. C. CHANDLEE, *J. Am. Chem. Soc.* **56**, 1278 (1934); see also F. W. ARNOLD and G. C. CHANDLEE, *ibid.* **57**, 8 (1935);·H. H. GEIST and G. C. CHANDLEE, *Ind. Eng. Chem., Anal. Ed.* **9**, 169 (1937).

[194] F. ZETSCHE and M. NACHMANN, *Helv. Chim. Acta* **9**, 420, 705, 979 (1926).
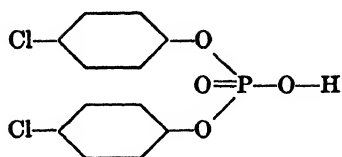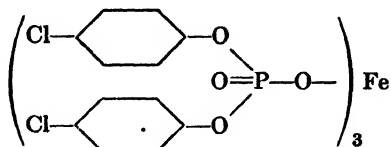
(I)   (II)

Only the ferric salt has been studied thoroughly. As shown by (II), it is characterized by its large volume requirements, and by the great weight of the three acid radicals attached to the iron atom. This salt comes down as a light yellow, voluminous precipitate when an alkali chlorophenylphosphate is added to a 2 N hydrochloric acid solution of a ferric salt. After washing with 40% alcohol to remove the coprecipitated free acid, and drying, the salt is ready for weighing. With only 5.53% iron, it contains less of this metal than most other weighing forms.[195] This precipitation of iron is specific in the presence of metal ions that form acid-soluble crystalline chlorophenylphosphates. In the presence of chromium and aluminum, which are precipitated to only a slight extent in 2 N hydrochloric acid, the mixed precipitate must be decomposed by treatment with ammonia. The resulting hydrous oxides are taken up in acid, and the precipitation is repeated. It is not possible to determine iron accurately by this method if lead, mercury, or stannic salts are present. Despite these limitations, the behavior of bis-p-chlorophenylphosphoric acid exhibits a striking selectivity.

[195] In gravimetric procedures, considerable advantages are offered by weighing forms that contain low percentages of the constituent being determined. The unavoidable mechanical and weighing errors are greatly diminished because of the favorable conversion factor. Consequently, organic precipitants that lead to mixed organic-inorganic precipitates and weighing forms are very desirable, particularly if their use also contributes to specific and selective precipitation. Such organic precipitants are especially valuable in the microgravimetric determination of inorganic materials. In these procedures, precipitation, filtration, washing, and weighing on a micro scale are often the only means of making quantitative determinations on very small samples. It is clear that the experimental errors in such cases become increasingly significant when the weighing form contains higher percentages of the material being determined. Organic-inorganic weighing forms thus decrease the unavoidable analytical errors. In certain cases, namely at extremely low percentage contents, micro quantities of a dissolved material can produce so much precipitate, that it can be filtered, washed, and weighed by macro methods. The precipitation of iron by means of bis-p-chlorophenylphosphoric acid is a striking instance of the points discussed here. Other instances are calcium picrolonate, $Ca(C_{10}H_7O_5N)_2 \cdot 8H_2O$, containing 5.64% calcium, and uranyl zinc sodium acetate, $(UO_2)_3ZnNa(C_2H_3O_2)_9 \cdot 6H_2O$, with 1.5% sodium. Another example is the familiar ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$. This purely inorganic complex compound contains only 1.6% phosphorus.

This precipitant has not received much consideration as a reagent for iron because of the ready availability of other sufficiently sensitive and selective color reagents, which are also suitable for quantitative determinations. Nevertheless, the reagent ·could probably render valuable aid in solving special problems. An example is the analysis of inks, where the iron can be precipitated directly in the presence of hydrogen peroxide. (The latter serves to oxidize the ferrous tannate.) The following properties of the iron salt deserve consideration in view of further possible applications, and because its study serves to extend the present knowledge of metallo-organic compounds. The precipitate is absolutely resistant to ammonium thiocyanate and hydrogen ˙sulfide. Potassium ferrocyanide reacts slowly to give Prussian blue. Protracted washing with hot water causes gradual hydrolysis, as shown by a change from light yellow to brown. Accordingly, the salt is readily converted to $Fe_2O_3 \cdot xH_2O$ by ammonia or a fixed alkali, and the freed acid goes into solution in the form of its alkali salt. A precipitate that has been washed with water is very easily peptized by 90% alcohol and forms a suspension that passes through the filter. If the iron salt is precipitated at room temperature, the fresh material will dissolve in 2% hydrochloric acid. Aged preparations, or those that have been precipitated from warm solutions in the presence of ammonium salts, require concentrated hydrochloric acid to effect their solution.

It is quite likely that other applications of this reagent will be found. Although no studies have been made, obvious possibilities are Bi^{+++} and Zr^{++++} ions, which yield very acid-stable phosphates. The reagent precipitates amines from acetic acid solutions, and likewise flocculates gelatin and other protein solutions. Consequently, it would be interesting to explore the possibilities of using bis-*p*-chlorophenylphosphoric acid for the detection and determination of polyatomic organic bases, especially alkaloids and dye bases, and certain degradation products of proteins.

Zetsche and Nachmann (*loc. cit.*) studied the action of numerous aliphatic and aromatic mono- and diesters of phosphoric acid toward acidified solutions of ferric ions. The aliphatic mono- and diester acids were found to be inactive. Accordingly, a definite weighting effect of the aromatic radicals is evident. Among the diester acids of the phenols, the phenyl-, β-naphthyl-, *o*-chloro-, and *p*-bromo-compounds behave like the bis-*p*-chlorophenylphosphoric acid. It is remarkable that the bis-anilido- and also the bis-trichlorophenylphosphoric acid do not form acid-stable ferric salts. This latter example emphasizes the fact that caution must be exercised in expecting that the mere weighting of an acid organic reagent by introducing halogen atoms will necessarily lead

to salts with lower solubility and increased resistance to acids (see Chapter IX, p. 416). The available studies and data are not sufficient to warrant any reasonably certain predictions concerning the effect of halogen substitution in organic reagents.   .

The Specific Action of the Acidic —O—OH Group

The instances of specific or selective action of definite groups discussed thus far involved organic compounds. In these, it is possible to specify the characteristic groups of the molecule far more often than when inorganic reagents are under consideration. A specific action of the —O—OH group, which frequently is a constituent both of inorganic and of organic peracids, will be described. The experiments that led to the establishment of the special action of this group were based on the very important studies by Abel[196] of the catalytic action of molybdic acid on the reaction between hydrogen peroxide and sodium thiosulfate in acetic acid solution. He showed that the reaction which normally proceeds:

$$2S_2O_3^{--} + H_2O_2 + 2H^+ = S_4O_6^{--} + 2H_2O \tag{1}$$
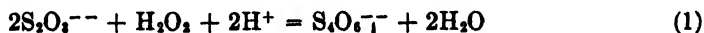
follows an entirely different course if molybdates are present. The product then is not tetrathionate, but sulfate:

$$S_2O_3^{--} + 4H_2O_2 = 2SO_4^{--} + 2H^+ + 3H_2O \tag{2}$$
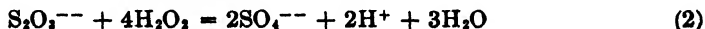
The activity of the molybdenum is due to the formation of permolybdic acid (or its anions), which react with thiosulfate in a manner different from that of free hydrogen peroxide. The effect of the molybdenum can be termed catalytic, since, after the reaction between the permolybdate and the thiosulfate ions, normal molybdate ions are regenerated which again produce MoO_5^{--} ions with the hydrogen peroxide. Consequently, this is a typical instance of intermediate reaction catalysis (compare Chapter IV). If it is remembered that a catalyst can never magically produce a reaction, but merely speeds up an existing reaction, then it must be assumed that hydrogen peroxide can react with thiosulfate according to (1) as well as (2). However, reaction (2) proceeds so sluggishly in neutral or weakly acidified solutions that it is practically unobservable. Under the present experimental conditions, it comes into being only because molybdenum intervenes in the course of the reaction through the continuous production and reaction of peroxymolybdate. The catalytic effect of molybdenum can be strikingly demonstrated if molybdate is added to a thiosulfate solution that also contains barium chloride, hydrogen peroxide, and acetic acid. Since barium sulfate is far less soluble than barium thiosulfate or tetrathionate, the occurrence

[196] E. ABEL, Monatsh. 34, 821 (1913).

of reaction (2) is unmistakably revealed by the precipitation of the sulfate, provided certain concentration relationships are maintained, and if a blank is run for comparison purposes. Abel[197] recommends the use of a freshly prepared mixture of equal volumes of the following solutions: (a) 1 g. $Na_2S_2O_3 \cdot 5H_2O$ in 100 ml. water; (b) 0.6 g. $BaCl_2 \cdot 2H_2O$ in 100 ml. $N/20$ acetic acid. The mixture remains perfectly clear for about 15–20 minutes after the addition of water (blank). Treatment with a very dilute solution of molybdate results in a precipitate or turbidity ($BaSO_4$) after a much shorter time. Mere stirring with a molybdenum wire suffices to precipitate barium sulfate, a very impressive demonstration.

In view of the rule, particularly stressed in this chapter, that the occurrence of reactions is related to the presence of certain atomic groups in organic reagents, it was logical to expect that the activation of hydrogen peroxide, discovered by Abel, would not be limited to molybdenum, but would occur with all metals and non-metals which, analogous to molybdenum, are capable of forming peroxo-acids, *i.e.*, compounds containing the group —O—OH. Actual trials showed[198] that tungsten, vanadium, titanium, zirconium, and thorium salts behave similarly to the molybdates. Furthermore, it was found that thiosulfate is oxidized to sulfate by peroxyformic, peroxyacetic, and peroxyphosphoric acid, or their salts. Somewhat later, Komarowsky and Schapiro[199] found that niobium and tantalum show an analogous reaction, a finding that could have been predicted since these elements also form peroxy compounds. Obviously then, the activation of hydrogen peroxidere presents a group effect. The effect is in contrast to the examples of specific or selective group actions in organic reagents cited earlier in this chapter. When hydrogen peroxide is activated, the reactive —O—OH group bound to the metal atom is formed at the particular time in the reaction medium, where it is consumed and regenerated. This succession of events corresponds to the mechanism of an intermediate reaction catalysis. Consequently, extremely small quantities of metallic peroxyacid-formers can be detected through the formation of the reactive —O—OH group. The identification limits and concentration limits given in the following table were obtained by mixing 4 ml. of the neutral test solution with an equal volume of the foregoing Abel reagent solution:

0.2γ niobium (1:20,000,000)	1.0γ vanadium (1:4,000,000)
0.4γ tantalum (1:10,000,000)	0.5γ titanium (1:8,000,000)
1.0γ molybdenum (1:4,000,000)	1.0γ zirconium (1:4,000,000)
2.0γ tungsten (1:2,000,000)	1.0γ thorium (1:4,000,000)

[197] E. ABEL, *Z. Elektrochem.* **19**, 480 (1913).
[198] F. FEIGL, *Z. angew. Chem.* **44**, 731 (1931).
[199] A. KOMAROWSKY and M. SCHAPIRO, *Mikrochim. Acta* **3**, 144 (1938).

The activation of hydrogen peroxide by the metals included in the table was ascribed to the production of acidic —O—OH groups as a result of the condensation of the metal compounds with hydrogen peroxide. The existence of such compounds is confirmed by the constitution of peroxomolybdic and peroxotungstic acid (I). It was pointed out in Chapter, IV in the discussion of the masking action of hydrogen peroxide, that peroxy compounds of another type are known. Thus Meyer and Pawletta[200] demonstrated that, in acidified vanadate solutions containing hydrogen peroxide, there are ions of peroxovanadium salts (II) as well as of its hydrolysis product, peroxoorthovanadic acid (III).

$$
\begin{array}{cccc}
\underset{(\text{I})}{\overset{\displaystyle O}{\underset{\displaystyle O}{>}}\!Mo\!\overset{\displaystyle O-OH}{\underset{\displaystyle OH}{<}}}
&
\underset{(\text{II})}{\overset{\displaystyle O}{\underset{\displaystyle O}{|}}\!>\!VX_2}
&
\underset{(\text{III})}{\overset{\displaystyle O}{\underset{\displaystyle O}{|}}\!>\!V\overset{\displaystyle OH}{\underset{\displaystyle OH}{-}}}
&
\underset{(\text{IV})}{O=V\overset{\displaystyle O-OH}{\underset{\displaystyle OH}{<}}}
\end{array}
$$
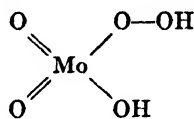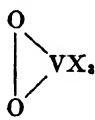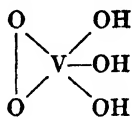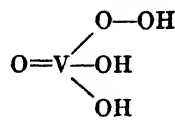
Titanium compounds of analogous structure exist. Furthermore, instances are known of metal-peroxy compounds whose molecules include oxygen bridges such as those shown in (I) and (II). Since vanadium salts behave toward the system H_2O_2—$Na_2S_2O_3$ as peroxymolybdic (tungstic) acid does, the following alternatives present themselves. Either a univalent —O—OH group behaves like a divalent —O—O— group, or an —O—O— group, in the simultaneous presence of an OH group, is capable of rearranging to produce an isomeric compound containing an —O—OH group. Compare (III) and (IV).

The activation of hydrogen peroxide in the present circumstances in all likelihood is due to the production of the univalent —O—OH group, rather than the divalent —O—O— group. Support for this statement is provided by a comparison of the influence of molybdenum, vanadium, and titanium salts on the reaction between arsenious acid and hydrogen peroxide in the presence of mineral acid.[201] The reaction, which can be summed up: $AsO_3^{---} + H_2O_2 \rightarrow AsO_4^{---} + H_2O$ is not instantaneous, but proceeds at a measurable rate. This can be shown by means of an acidified hydrogen peroxide solution containing an excess of As_2O_3, from which portions are removed from time to time, and tested for hydrogen peroxide by adding a molybdenum, vanadium, or titanium salt. Colored peroxy compounds are produced, but the resulting yellow, red, or yellow-brown colorations become progressively weaker. In a mixture made up from 0.5 ml. 3% H_2O_2, 1 ml. 2 N HCl, and 1 ml. 1 N Na_2HAsO_3 the reaction is completed within approximately 12 minutes; at least, the solution

[200] J. Meyer and A. Pawletta, Z. anal. Chem. 69, 15 (1926).
[201] F. Feigl and I. D. Raacke, Unpublished studies.

no longer responds to the rather delicate "pertitanate test" for hydrogen peroxide. If comparison experiments are made by treating a mixture of 0.5 ml. 3% H_2O_2, 1 ml. 2 N HCl, and several drops of a strong molybdate, vanadate, or titanium salt solution, respectively, with 1 ml. 1 N Na_2HAsO_3 the following will be observed. The color in the molybdate mixture will be completely discharged after 1 or 2 minutes. This signifies that the original hydrogen peroxide, which was transformed by the molybdenum into peroxymolybdic acid, is consumed in even this brief time in the oxidation of the arsenious acid. The color of the mixture containing vanadium is slightly lessened after about 30 minutes, and this fading continues very slowly; even after 6 hours, the color does not reach that of an acidified, hydrogen peroxide solution which contains no vanadium. The lightening of the color begins later in the titanium-bearing solution, and its complete discharge requires several hours. Excess formaldehyde reacts analogously to arsenious acid with respect to acidified hydrogen peroxide solutions containing molybdenum, vanadium, or titanium. In this instance also, the solutions containing vanadium or titanium will retain their color after the molybdenum-bearing solution has faded completely. These experiments, therefore, demonstrate indubitably that, in mineral acid solution, peroxymolybdic acid, which contains the —O—OH group, displays a greater oxidizing power than hydrogen peroxide. In contrast, both peroxyvanadic and peroxytitanic salts, which have —O—O— groups bound to the metal atom, surprisingly have a much lower oxidation capability than hydrogen peroxide. Hence, it may be stated that molybdenum activates the system: H_2O_2—As_2O_3—H^+, whereas vanadium and titanium deactivate (inhibit) this redox mixture.

It was pointed out on p. 125 that molybdic and tungstic acid catalytically accelerate the reaction of hydrogen peroxide and I^- ions. This reaction, which liberates iodine, normally goes quite slowly in strongly acidified solutions. An entirely analogous effect is exercised by these metallo-acids on the reaction between hydrogen peroxide and Br^- ions; free bromine is produced.[202] Titanium salts have no effect on this redox reaction. Vanadates do activate the hydrogen peroxide, but to a much lesser extent than molybdate or tungstate. The activation of hydrogen peroxide by vanadium obviously is due to the fact that the acidified solution contains not only the inactive peroxy salt form (III) but also (and perhaps in equilibrium) small amounts of the active peroxyacid form (IV).

The foregoing discussion indicates that the activation of hydrogen

[202] F. FEIGL and V. DEMANT, unpublished studies. Compare also V. DEMANT, Dissertation, Vienna, 1937.

peroxide is a group effect. However, the group —O—OH, which is regarded by the author as essential, is also present in hydrogen peroxide if it has the usually accepted structure H—O—O—H. Consequently, the question arises as to what constitutes an activation. A natural thought in this connection is the fact that hydrogen peroxide itself is a very weak electrolyte, namely, it is a very weak acid. Its acidic character comes distinctly to light only in its alkali salts, and the occurrence of HO—O⁻ ions becomes significant only in alkaline solutions. The anions of the metallo-peroxyacids are merely derivatives of this anion, in which radicals containing molybdenum, tungsten, *etc.*, have replaced the H atom. It is quite enlightening that such substitution markedly increases the acidic character of hydrogen peroxide. Consequently, when dealing with peroxyacids, the appearance of such substituted anions can be counted on, even in acid solutions. If the activation is ascribed to the production of such substituted anions, then it is logical to expect that even pure hydrogen peroxide solutions must be "activated" on alkalization. This actually occurs, since it is well known that hydrogen peroxide is much more active in basic solution than in a neutral or acid medium. For example, the oxidation of thiosulfate to sulfate, or of arsenite to arsenate, has to be catalyzed when peroxyacid-formers are used in acid solution, but these reactions proceed smoothly and without a catalyst in basic media. This finding is in entire agreement with the postulation that the concentration of active HO—O⁻ ions is raised by alkalization. It is logical to expect that the strength of the base used to alkalize the solution must play a role, and that hydrogen peroxide solutions made alkaline with sodium or potassium hydroxide will contain a higher concentration of HO—O⁻ ions and hence have greater oxidizing power than ammoniacal peroxide solutions. This expectation has been fulfilled. For instance, ammoniacal thallous solutions are not affected by hydrogen peroxide, whereas, in the presence of strong bases, oxidation occurs at once and dark brown thallic oxyhydrate precipitates. The following observations[203] are quite striking and informative. If a clear ammoniacal hydrogen peroxide-thallous solution is treated with several drops of a zirconium, thorium, niobium, or tantalum salt solution,[204] there is an immediate precipitation of not only the insoluble peroxy compound of the particular added metal, but black thallic oxide also comes down at once. This signifies that hydrogen peroxide can be activated even in ammoniacal solution by peroxyacid-formers, and not merely in acid solution. This

[203] F. FEIGL and I. D. RAACKE, unpublished studies.
[204] Mo, W, V, and Ti salts are not suitable for these experiments, because insoluble thallium salts (probably of the respective peroxyacids) are formed under the prescribed conditions.

activating effect in ammoniacal solution is exhibited still more strikingly in the oxidation of certain indicators. Ammoniacal solutions of methyl orange or phenolphthalein remain yellow and red, respectively, for a long time after hydrogen peroxide is added, and even warming the mixture has no effect. However, complete decolorization, within a few minutes, follows the introduction of a few drops of a Mo, W, V, Zr, Th, Ti, Nb, or Ta salt solution. The analogy between the oxidation of these coloring matters with that of thallium is also shown by the fact that their alkaline solutions likewise are decolorized rapidly by hydrogen peroxide without the intervention of a catalyst. Consequently, the available concentration of HO—O$^-$ ions is adequate to accomplish the destructive oxidation of these indicators. Also in harmony with the supposition that the activation of hydrogen peroxide is due to the production of HO—O$^-$ ions or their substitution products, is the aforementioned fact that hydrogen peroxide, in acid solution, is deactivated by titanium or vanadium salts. This inhibitory effect is obviously brought about by the binding of the —O$_2^-$ group on the metal atom. The consequence is a decrease in the concentration of hydrogen peroxide and hence the original low concentration of HO—O$^-$ ions is lowered still more.

Selective Actions Exercised by Organic Derivatives of Ammonia

All the very numerous basic organic derivatives of ammonia possess a common property: the ability to enter into addition reactions with acids and metal salts. They thus plainly exhibit their derivation from ammonia. This general behavior, however, also indicates that not too much should be expected of these materials with regard to extensive selectivity. The addition of acids results in organic derivatives of ammonium salts; the addition to metal salts gives rise to ammine compounds of the intercalation and addition compound types. An important role in such addition reactions is played by the nature of the organic radicals that have replaced the hydrogen atoms of the ammonia; the molecular volume and weight of the radicals are of fundamental significance. It may be taken as a rule that acids which produce ammonium salts that are but slightly soluble in water are predisposed also to form difficultly soluble salts with organic bases. However, slight solubility is often encountered among salts of organic bases with acids that produce soluble ammonium salts. Insolubility of ammonium-like salts of organic bases is never solely dependent on the volume and weight of the base; the nature of the organic component is always a factor. Thus, salts of water-insoluble organic bases with halogen hydracids and monobasic oxyacids are, with very few exceptions (see p. 305), quite soluble in water. This solubility is important because, if the need arises, insoluble bases can be

used in the form of their soluble hydrochlorides.   The solubilities of the
hydrohalides of an organic base (B·HCl; B·HBr; B·HI) decrease with
rising weight and increasing volume of the halogen atom.   Practically
all of the hydropolyiodides of bases, *i.e.*, the salts of polyiodohydracids
(B·HI·I$_x$) are quantitatively insoluble.   It is, therefore, evident that
the weight and volume of the anionic component of the salt exert a
dominant influence on the solubility of salts.   In agreement with this is
the fact that mono- and dibasic complex metallo-halogen acids such as
H[BiI$_4$], H$_2$[HgI$_4$], H$_2$[Hg(CNS)$_4$], can function as general precipitants
for organic bases of high atomicity.   This effect, used in reverse, makes
possible selective tests and quantitative methods for those metals that
have the ability to produce complex acido anions.   In such cases, a
quantitative precipitation can often be accomplished by merely treating
a metal salt solution with an alkali salt of a complex-forming acid together
with an excess of the hydrochloride of a polyatomic base.   This principle
is the basis of a number of interesting newer procedures for the determina-
tion of metals.[205]   It is obvious that the percentage content of metal in
the precipitate can be greatly decreased by employing bases and com-
plex-forming ions with high molecular or radical weights.   Numerous
possibilities are open along this line in view of the wide choice among
available organic bases.   However, marked selectivity can only be
anticipated if pH relationships or masking effects exist and can be
utilized.

The influence of size and weighting effects among organic derivatives
of ammonia becomes evident not only in the insolubility of compounds
of the type of ammonium salts but also in molecular compounds with
metal salts that correspond to the·type of ammine salts.   Insoluble
addition compounds predominate among these, but soluble and insoluble
intercalation compounds of this type are known.[206]

The ability of nitrogen bases to form salts and to coordinate is greatly
influenced by any organic radicals attached to the nitrogen atoms, or by

[205] Instances are the precipitation of hydroxyquinoline salts of phosphomolybdic
acid and hydroiodobismuthic acid for the determination of phosphate and bismuth.
See R. BERG, *Z. angew. Chem.* **41**, 611 (1928); R. BERG and O. WURM, *Ber.* **60**, 1664
(1927).   Other examples are the quantitative determination of cadmium and bismuth
by precipitation of the corresponding hydroiodo acids with α- or β-naphthoquinoline
("naphthine").   See R. BERG and O. WURM, *Ber.* **60**, 1664 (1927); F. HECHT and
R. REISSNER, *Z. anal. Chem.* **103**, 88´(1935).
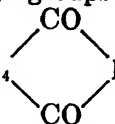
[206] G. SPACU and his coworkers have worked out numerous quantitative methods
for determining metals.   These procedures are based on the production of insoluble
complex salts with pyridine, ethylenediamine, propylenediamine, benzidine, and
toluidine as the neutral component.   The literature is given in F. J. WELCHER, *op. cit.*
VAN NOSTRAND, New York, 1947-1948.

groups introduced into these radicals.   Furthermore, not only primary, secondary, and tertiary amines, but also polyamines, and likewise bases with cyclic bound nitrogen atoms, can be regarded as derivatives of ammonia.   Consequently, the possibilities of variation are confusingly great.   Practically no regularities of analytical utility have been established, and there are few, if any, guiding principles to indicate which derivatives of ammonia are likely to furnish selective actions.   It is certain that replacement of hydrogen atoms in ammonia by alkyl groups alters the coordinative ability and basicity of the nitrogen atoms comparatively little in comparison with the effect produced by introducing aryl groups, which weaken these properties.   However, this is actually all that can be predicted.   Hence, empirical findings must be relied on almost exclusively.   They indicate that interesting analytical effects may be sought among aliphatic, aromatic, and cyclic 1,2- or *ortho*-diamines, because they can be built into 5- and 6-membered rings by salt formation and coordination.   It is known that steric factors can play an important role in determining selective actions when organic bases form salts (see pp. 309 and 315).

The analytical use of organic nitrogen bases, and also the study of selective actions, involve more than a consideration of the production of compounds of the types of ammonia and ammine salts.   An important influence is exercised also by the NH_2 and NH groups as well as cyclic bound nitrogen atoms that are situated in a coordinative position with respect to acidic groups.   The acidic character is usually weakened in such compounds but, as compensation, they offer the possibility of producing inner complex salts that may have analytical significance.   Pertinent examples have been cited in almost every section of this chapter, and additional uses of such inner complex-forming compounds will doubtless be discovered.   Basic groups in slightly soluble organic compounds that also retain acidic groups may possess additional importance because they may function as solubilizing vehicles by forming salts with mineral acids.   Consequently, the introduction of basic groups into organic reagents is sometimes an aid in bringing about water-solubility in an acid medium.   Finally, it should be noted that basic groups, particularly $N(CH_3)_2$ frequently exert chromotropic or auxochromic effects.   They also may influence the coordinative ability of other groups.   All these items may be of great significance in enhancing the selective action of organic reagents.

The NH group deserves special consideration.   It is generally known that the basic character of primary and secondary amines is markedly decreased when negative groups are introduced into them.   The linking

of an NH_2 or NH group with acyl groups may so loosen H atoms that

acids result.   Examples are C_6H_4 ⟨CO／NH／CO⟩ NH and $C_6H_5SO_2NH_2$.   The

replaceability of the H atom of acidic NH groups by silver (often by mercury) seems to be characteristic.   This finding has turned attention to cyclic compounds in which an NH group is directly bound to both a CO and a CS group.   Such compounds have proved to be silver-selective, and a representative of this class was the first sensitive, organic color reagent for silver (see p. 328).

Acidic imide groups with no adjacent CO or CS groups are found in imidazole[206a] and its derivatives, e.g., benzimidazole[206b] and benzotriazole.[206c]   The common feature of these compounds is that the NH group is incorporated in the ring $HN\langle$ ▭ with N atoms in the 2 or 3 (or 2 and 3) positions.   The acidifying influence of the double bonds is so marked that these compounds form insoluble salts not only with Ag and Hg, but also with divalent metals, and in many cases even in ammoniacal solution.

This discussion of selective actions exhibited by organic derivatives of ammonia would be incomplete without a brief reference to the behavior of aromatic p,p'-diamines and their alkyl products.   When treated with suitable oxidants, they are easily converted into colored quinoidal products.   This change does not involve salt-formation; it is the result of redox reactions stemming from the tendency of aromatic ring systems bound to nitrogen to form quinones.   Reactions of this type sometimes can be used to advantage for analytical purposes, especially when there is a distinct pH relationship with respect to the oxidation and hence a likelihood of selectivity.

Organic Bases that Form Water-Insoluble Nitrates

In general, chlorides and nitrates of organic bases are soluble in water. Accordingly, water-insoluble weak bases, such as alkaloids and dyestuff bases, can easily be brought into solution by treatment with dilute hydrochloric acid.   This expedient is frequently resorted to in organic analysis to separate basic compounds from neutral substances and organic acids. Organic bases that produce difficultly water-soluble salts with nitric acid are therefore striking exceptions to the general rule.   The following bases

[206a] E. J. FISCHER, Wiss. Veröffentl. Siemens-Konzern 4, 171 (1925).
[206b] F. FEIGL and H. GLEICH, Monatsh. 49, 385 (1928).
[206c] J. A. CURTIS, Ind. Eng. Chem., Anal. Ed. 13, 349 (1941).

are known to form slightly soluble nitrates: cinchonamine (I)[207]; diphenyl-endanilodihydrotriazol (II)[208]; di-1-naphthyldimethylamine (III)[209]; α-phenyl-β-diethylaminoethyl-p-nitrobenzoate (IV)[210]; N-diethylbenzo-hydrylamine (V):[211]
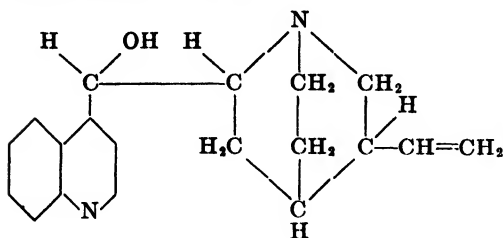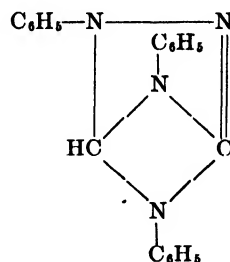
(I)   (II)
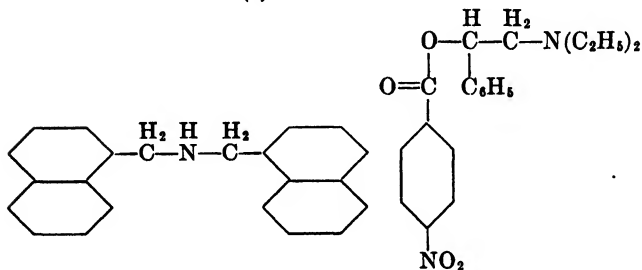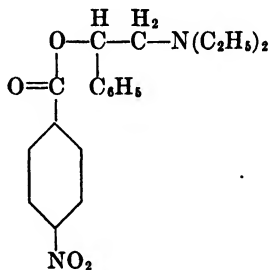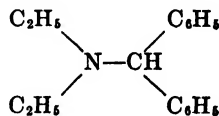
(III)   (IV)   (V)

Only (II), which is familiarly known as "nitron," has been used to any extent in inorganic or organic analytical practice. One study has been published on the use of (III) for the quantitative determination of nitrate. Nevertheless, it seems appropriate to include certain statements regarding the precipitation of nitrate by means of these five bases in the present discussion of the action of organic reagents as consequences of the presence of certain atomic groupings. First of all, the mere existence of these nitrate precipitations shows that organic reagents can give results that have no counterparts in the action of inorganic reagents. Consequently, the prospect is by no means hopeless of discovering organic reagents that will aid materially in solving such difficult problems as the precipitation and separation of the alkaline earth and alkali metals. This is the pleasant aspect presented by the precipitation of nitrate by means of organic bases. The other side of the picture is not

[207] M. ARNAUD, Compt. rend. 97, 174 (1884); 98, 1488 (1884). Compare O. HESSE, Ann. 225, 211 (1884) and P. GAMMARELLI, Gazz. chim. ital. 22, 635 (1893).

[208] M. BUSCH, Ber. 38, 861 (1905).

[209] H. RUPE and P. BECHERER, Helv. Chim. Acta 6, 674 (1923).

[210] C. S. MARVEL and V. DU VIGNEAUD, J. Am. Chem. Soc. 46, 2661 (1924).

[211] A. OGATA and M. KONISHI, J. Pharm. Soc. Japan 54, 546 (1934).

so pleasing. A review of the nitrate-precipitating bases reveals how very little really sound foundation exists on which to construct forecasts of analytically useful reactions, particularly precipitation reactions for anions. Purely empirical trials are almost the only method of attack. Admittedly, the available knowledge does not suffice for the unassailable prediction of the degree of insolubility or intensity of the color that will be exhibited by the products obtained with other organic reagents. However, many of the examples of specific and selective organic reactions cited in this chapter prove that analytical activity can be attributed to definite atomic groupings. Accordingly, an acquaintance with the salt-forming capabilities of such groups often makes it possible to enhance the selectivity and sensitiveness of the reagent by judiciously introducing other groups. This statement does not hold for any of the compounds (I) to (V). All that is known is that they form salts by adding nitric acid, or its hydrogen atom, to a nitrogen atom and so produce ammonium-like compounds. But nothing authoritative can be stated as to which groups in the molecule of the base are responsible for the lowered solubility of the salt that follows a dissociation and hydration of its polar component. An inspection of the structural formulas (I) to (V) shows that these organic bases are of quite different kinds and the only things they have in common are high molecular weight and large molecular volume. However, other organic bases with these characteristics form soluble nitrates, and so at present there are no guiding principles as to which organic bases offer any prospect of providing nitrate-precipitating reagents.

Bases (I) to (V) are all monoacidic, but their precipitating action with nitrate is only selective since other acid radicals also may form slightly-soluble salts with these reagents (see below). It is noteworthy that sulphate forms no precipitate with these bases, even though the sulfates of many polyatomic organic bases are difficultly soluble. Consequently, the particularly important practical precipitations with nitron and di-1-naphthyldimethylamine are usually carried out in the presence of sulfuric acid.

The nitrate precipitate produced by nitron can be seen at a dilution down to 1:60,000 at room temperature, and down to 1:80,000 at 0°C. Although these sensitivities do not equal the corresponding figures of other organic precipitants, nitron, nevertheless, renders excellent service, particularly in gravimetric determinations of nitrate. These determinations can be accomplished with considerable accuracy, provided the solution contains at least 100 mg. of HNO_3. The marked solubility of nitron nitrate is offset in these determinations by the fact that the precipitate, after drying at 110°C., contains only 16.8% HNO_3, and

hence the conversion factor is quite favorable.   Furthermore, the solubility is greatly decreased if excess soluble nitron salts are present. Finally, the precipitate always contains occluded nitron, and this contamination compensates for the error arising from incomplete precipitation.[212]

Nitron and di-1-naphthyldimethylamine, which will be discussed presently, are among the few organic compounds whose synthesis, salt-forming ability, and use as an analytical reagent were all described by a single author.   Busch (*loc. cit.*) showed that the following acids form precipitates with nitron at the respective dilutions:

HBr	1:800	$HClO_4$	1:50,000
HI	1:20,000	H_2CrO_4	1:6,000
HCNS	1:15,000	HNO_2	1:40,000
$HClO_3$	1:4000	Picric acid	1:250,000

Consequently, when other acids are present, the direct detection and determination of nitric acid is possible only within certain limiting proportions.   Most of these interfering anions can be removed by precipitation with lead acetate.   Nitrite is easily destroyed by treatment with hydrazine sulfate, sodium azide, or sulfamic acid.   It is not possible to separate perchloric acid, whose precipitation of the nitron salt, at room temperature, has about the same sensitivity as the nitrate precipitation.   It should also be noted that all of the organic bases which form slightly soluble nitrates also produce slightly soluble perchlorates. Nitron can therefore be used to determine perchlorate gravimetrically.[213] This reagent lends itself well to the speedy solution of certain difficult problems encountered in organic analysis.   Some of these uses were developed by Busch.[214]   Typical examples are: the determination of picric acid and its separation from dinitrophenols; the differentiation of organic nitrates from nitro compounds (*e.g.*, urea nitrate and guanidine nitrate from nitrosourea and nitrosoguanidine); the elegant determination of nitrocellulose, based on the precipitation of the nitrate that is formed by saponification of nitrocellulose by means of alkali and hydrogen peroxide.[215]   Geilmann and his collaborators[216] used nitron in the determination of rhenium.   If mixed with other metals, the rhenium is

[212] L. B. WINKLER, *Z. angew. Chem.* **34**, 46 (1921) made a very interesting study of the quantitative determination of nitrate by means of nitron, and established the most favorable conditions for the procedure.

[213] A. VUERTHEIM, *Rec. trav. chim.* **46**, 97 (1927).

[214] M. BUSCH and G. BLUME, *Z. angew. Chem.* **21**, 354 (1908).

[215] C. COPE and J. BARAB, *J. Am. Chem. Soc.* **39**, 504 (1917) have given an excellent survey of the applications of nitron in quantitative organic and inorganic analysis. See also, J. HECK, H. HUNT and M. G. MELLON, *Analyst* **59**, 18 (1934).

[216] W. GEILMANN and A. VOIGT, *Z. anorg. allgem. Chem.* **193**, 311 (1930); W. GEILMANN and F. WEIBKE, *ibid.* **195**, 289 (1931); **199**, 347 (1931).

precipitated initially as sulfide, which is then converted to perrhenate by treatment with alkali and hydrogen peroxide. The solution is then acidified with sulfuric acid and the ReO_4^- ion is thrown down by nitron. The nitron perrhenate is dried and weighed. Here again the solubility of the precipitate is strikingly lowered by the presence of nitron acetate.

The extensive utilization of nitron is in sharp contrast to the limited application of di-1-naphthyldimethylamine (III). The single successful employment has been reported by von Konek.[217] This reagent is less selective than nitron, since its iodide, bromide, chlorate, bromate, and perchlorate are but slightly soluble; even the hydrochloride is only 0.1% soluble in water. Nevertheless, the reagent merits more consideration. With nitric acid it has a precipitation sensitivity of 1:170,000, which is about three times as great as the corresponding value for nitron. In addition, the precipitate and the weighing form contain 17.5% HNO_3, which is only slightly more than the 16.8% HNO_3 carried by the nitron salt. Di-1-naphthyldimethylamine, like nitron, is a precipitant for perchloric acid. In all likelihood, it too will be found suitable for the gravimetric determination of perrhenate. It has the advantages of being more readily obtained than nitron, and it is cheaper.

The isomeric di-2-naphthyldimethylamine forms no slightly soluble salts, either with nitric or other acids. This is a good example of the influence of the steric configuration of bases on the solubility characteristics of their salts. Finally, it should be pointed out, that the synthesis worked out by Rupe and Becherer (*loc. cit.*) should be adaptable to the preparation of derivatives of their reagent. Special interest would be attached to the derivatives containing halogen-substituted naphthyl groups, because the weighting effects would probably influence the sensitiveness of the nitrate precipitations advantageously.

The water-soluble salts of nitron and other nitrate-precipitating bases might be expected to exert a precipitating action, in acid solution, toward voluminous anions, especially complex anions. This would be in conformity with the rather common precipitability of large volume bases (*e.g.*, alkaloids) by large volume acids. The precipitating action of the voluminous $Fe[\alpha,\alpha\text{-dip}]_3^{++}$ cations (see p. 323) also belongs in this category. The writer's own studies have revealed the following facts. A black-green precipitate is produced on adding nitron hydrochloride to solutions of ferric salts that have been treated with an excess of pyrocatechol, and which therefore contain complex ferripyrocatechol anions (see p. 363). Analogously, nitron hydrochloride gives a red precipitate with solutions of cobalt salts that contain excess nitroso-R salt, and in which, therefore, inner complex cobalt-nitroso-R-anions are present

[217] F. v. Konek, *Z. anal. Chem.* 97, 416 (1934).

(see p. 257).   In contrast, the blue solution, which contains the complex anion of trivalent iron with ferron (see p. 187) forms no precipitate with nitron hydrochloride.   The following compilation shows that nitron and $Fe[\alpha,\alpha\text{-dip}]_3^{++}$ ion behave differently toward the complex acids just cited:

Precipitant	Complex anions		
	Fe^{III}-pyrocatechol	Fe^{III}-ferron	Co-nitroso-R
Nitron hydrochloride..	+	−	+
$Fe[\alpha,\alpha'\text{-dip}]_3SO_4$..........	+	+	−

− = not precipitable from $N/10$ solution.
+ = precipitable from $N/10$ solution.

The preceding statements suggest the desirability of studies concerning the precipitability of complex acids (i.e., acid-stable inner complex anions) by nitron and other nitrate-precipitating bases, and also by $Fe[\alpha,\alpha'\text{-dip}]_3^{++}$ ions.   It may be expected that new selective precipitation actions will be discovered by such investigations.

Selective Behavior of p-Fuchsine

West and Amis[218] found that p-fuchsine (or its hydrochloride) displays a selective action toward certain metal salts.   Only gold and palladium salts form precipitates with this triphenylmethane dye; platinum salts apparently react only in concentrated solution.   When a dilute solution of the reagent is used, the palladium precipitate is so finely divided that the occurrence of a reaction can be perceived by the fading of the dye solution.   If a blank is used for comparison, as little as 0.005γ Pd can be detected by this reaction carried out as a drop test on a spot plate.   The brown palladium salt has been isolated and analyzed. The empirical formula is $3\ PdCl_2 \cdot 2Fs$ (Fs = fuchsine monohydrochloride).

More interesting, perhaps, than the discovery of this new test for palladium is the elucidation of the constitution of the complex palladium-fuchsine compounds which it involves.   The starting point for this study, in the author's laboratory, by West,[219] was the fact that fuchsine is not only a monoacidic base as shown by the monohydrochloride formula (I), but may also add two more equivalents of acid to the remaining amino groups to form the trihydrochloride (II)

[218] P. W. WEST and E. S. AMIS, Ind. Eng. Chem., Anal. Ed. 18, 400 (1946).
[219] P. W. WEST, Anal. Chim. Acta 2, 133 (1948).

Fuchsine monohydrochloride   Fuchsine trihydrochloride
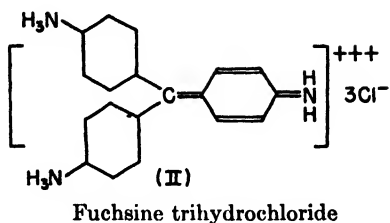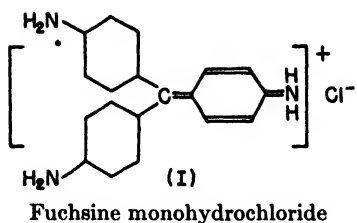
The hydrochlorides of organic bases can be regarded as substituted ammonium chlorides. From the standpoint of the coordination theory, ammonium salts present a coordination of hydrogen atoms of an acid on the nitrogen atom of the ammonia. The linkage of three molecules of hydrochloric acid to one molecule of the fuchsine base accordingly shows that the latter possesses three coordination positions by virtue of its three nitrogen atoms. It is known that $PdCl_2$ can coordinate two molecules of ammonia or primary amine, and hence the coordination formula (III) is indicated for the compound $3PdCl_2 \cdot 2Fs$. This coordinative representation shows an analogy to (II), insofar as one molecule of the dye base is linked with $1\frac{1}{2}$ molecules of $PdCl_2$ instead of with 3 molecules of HCl:

(III)

$3PdCl_4 \cdot 2Fs$
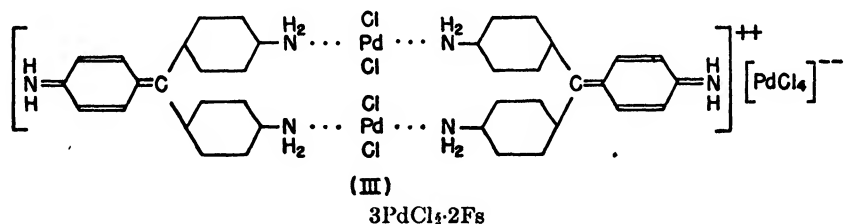
If representation (III) proved to be valid, it could logically be expected that $AuCl_3$ must also form an analogous compound, since one molecule of $AuCl_3$ by satisfying the coordination number of 4 is capable of adding one molecule of amine. The compound $3AuCl_3 \cdot 1Fs$ was actually isolated; coordination formula (IV) has been assigned to it. The compound $2AuCl_3 \cdot 1Fs$ also exists; it can be represented by (V):

(IV)
$3AuCl_3 \cdot 1Fs$

(V)
$2AuCl_3 \cdot 1Fs$
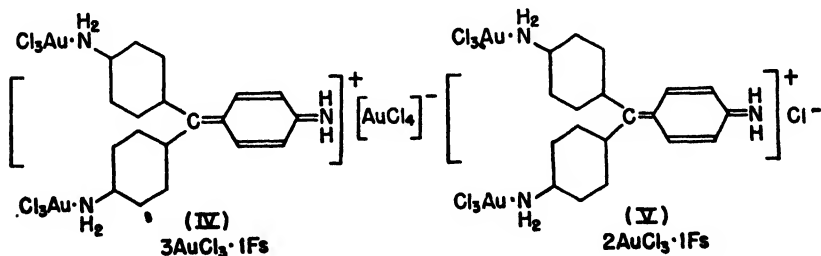
The coordination formulas (III) and (IV) represent complex compounds in which the NH_2 groups at one end of the dye molecule add molecules of noble metal chlorides, whereas the imido group at the other end, likewise by coordination, produces the cationic component of a salt of chloropalladic or chloroauric acid, respectively. Compounds of this type have not been known heretofore. A glance at their relatively complicated formulas would lead to the belief that they are not stable. The contrary is true as demonstrated by the ease with which the pure gold and palladium salts are quantitatively precipitated. The gold compound is so stable that it is not reduced to free gold even by hypophosphite. This fact permits the distinguishing of the gold and palladium salts, and therefore of a quite selective test for palladium.

It is rather remarkable that fuchsine derivatives, such as methyl violet, crystal violet and malachite green, in which the amino groups are methylated, react analogously to the parent dye with palladium and gold salts. However, the precipitation sensitivity with these derivatives is much lower than that of the parent fuchsine. The reason probably is that the binding of the noble metal salts is weaker in the N-methylated compounds. Consequently, the salts form only incompletely in aqueous solution and likewise suffer dissociation into their components there.

Selective Precipitations through Coordinative Binding of Benzidine

Benzidine, i.e., 4,4'-diaminodiphenyl (I), is a very weak base that is insoluble in water. Its water-soluble hydrochloride, nitrate, and acetate function as very selective precipitants, since only sulfate and tungstate are precipitated completely by them from mineral acid solution. More than a century ago, Zinin[220] noted the insolubility of benzidine sulfate, and 50 years later Vaubel[221] used the precipitation of this salt for the quantitative determination of benzidine. However, it was not until the opening of the present century that Mueller[222] and Raschig[223] used benzidine for the quantitative determination of sulfate. Several years later, von Knorre[224] showed that tungstate can be satisfactorily determined with the aid of benzidine hydrochloride. Accordingly, benzidine is among the earliest of the organic reagents that have been used in inorganic analysis.

Benzidine sulfate comes down as a white crystalline precipitate when sulfate solutions are treated with benzidine hydrochloride. Its composi-

[220] N. Zinin, J. prakt. Chem. 36, 95 (1845).
[221] W. Vaubel, Z. anal. Chem. 35, 163 (1896).
[222] W. J. Mueller, Ber. 35, 1587 (1902).
[223] F. Raschig, Z. angew. Chem. 16, 617 (1903).
[224] G. v. Knorre, Ber. 38, 783 (1905).

tion is accurately represented by (II). The bright yellow "benzidine tungstate," obtained in the same manner, is not analogous in composition; it contains more WO_3 than corresponds to a salt of the diacid base benzidine; furthermore the water content varies. Its composition[224a] is indicated by (III). It seems correct to include the tungstate precipitate among adsorption compounds (see Chapter X).
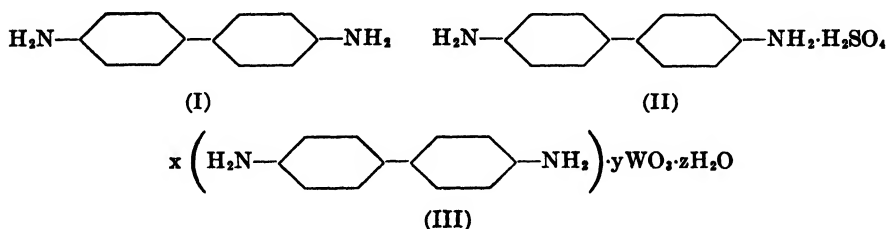
The sensitivity of the benzidine sulfate precipitation does not differ markedly from that of barium sulfate.[225] Consequently, at room temperature this reagent will not precipitate sulfate from solutions that have been masked against barium (e.g., chrom-sulfuric and other complex metallo-sulfuric acids).[225a] On the other hand, the precipitation sensitivity (1:100,000) of benzidine tungstate is much greater than the sensitiveness of the visible separation of WO_3·aq when alkali tungstate solutions are acidified (1:8,000). It also exceeds the sensitivity of the lead sulfate precipitation (1:25,000).

The analytical value of the benzidine precipitation of sulfate and tungstate lies primarily in the field of quantitative analysis. Because of its variable composition, the tungstate precipitate may not be weighed as such; it must be ignited to WO_3. Nevertheless, the complete precipitation of tungsten by benzidine is quite an asset, because, when tungstate solutions are merely acidified, only part of the WO_3 comes down, and the rest remains colloidally dispersed. Hence, the precipitation is not quantitative, nor will the suspension filter well, until the liquid has been taken to dryness several times, as in the determination of silica.

The precipitation of sulfate with benzidine may be handled in a variety of ways for quantitative purposes. (a) The benzidine sulfate can be weighed as such after drying at 105°C., (b) the freshly precipi-

[224a] M. TSCHILIKIN, Ber. 42, 1004 (1909) obtained $2C_{12}H_8(NH_2)_2$·$5H_2WO_4$ by the dropwise addition of Na_2WO_4 to a hydrochloric acid solution of benzidine.

[225] The analogy in the precipitating action of barium chloride and benzidine hydrochloride is not limited to sulfuric acid but extends to its organic derivatives. It appears that those sulfonic acids which form insoluble barium salts likewise produce insoluble benzidine salts.

[225a] P. JOB and G. URBAIN, Compt. rend. 170, 843 (1920).

tated salt can be washed free of acid and then titrated with standard
sodium hydroxide, using phenolphthalein as indicator; (c) the neutral
test solution of the sulfate can be treated with an excess of benzidine
hydrochloride, the precipitate filtered off, and the excess benzidine
hydrochloride in the filtrate then determined by titration with alkali.
These titrations are possible because the benzidine liberated from its
sulfate or chloride by a strong alkali is so weak a base that even its
saturated solution does not redden phenolphthalein.   Consequently,
benzidine sulfate, or chloride, can be titrated as though it were free
sulfuric, or hydrochloric, acid.   Unfortunately, only freshly precipitated
benzidine sulfate is rapidly decomposed by alkalies and hence susceptible
to smooth and quantitative titration.   The dried material has lost this
useful quality.   Benzidine sulfate, because of its high equivalent weight,
would be an excellent titrimetric standard provided it behaved similarly
to the fresh material, or if a variety should be discovered that would
react quickly even after drying.

There is an extensive literature on the precipitation of sulfate with
benzidine.[226]   The careful study by Haase[227] deserves special mention.
He made the surprising discovery that low values are obtained with
procedure (b) when magnesium salts are present.   Even relatively small
amounts of magnesium (150 mg./l.) produce considerable minus errors.
This deleterious effect has not been explained.

It is rather remarkable that only sulfuric and tungstic acids are
precipitated by benzidine from mineral acid solution.   Selenic acid,
which ordinarily behaves similarly to sulfuric acid, cannot be precipi-
tated by benzidine from mineral acid solution, but it will come down in
acetic acid solution.   The same is true of selenious acid.[228]   Tellurous
and telluric acids are not precipitable with benzidine.   Phosphates can
be precipitated from acetic acid solution; phosphoric acid acts as a
dibasic acid in this case.[229]   The precipitability of secondary alkali phos-
phate and arsenate by benzidine was observed by von Knorre (loc. cit.).

Pertusi[229a] discovered a reaction of benzidine that is very interesting
with respect to both analytical and complex chemistry.   He studied the
behavior of a mixture of benzidine acetate and mercuric succinimide
toward acetate-fluoride solutions.   A white precipitate results; it has the
empirical formula $2Bzd \cdot 4HF \cdot HgF_2$.   This reaction will reveal as little

[226] See F. J. WELCHER (op. cit.), Vol. 2, pp. 298, 307.

[227] L. W. HAASE, Z. angew. Chem. 40, 595 (1927).

[228] A. G. KRETOV, Chem. Abstracts 27, 42 (1933).

[229] A. DEL CAMPO, Chimie & industrie 23, 182 (1930); Chem. Abstracts 25, 473
(1931).

[229a] C. PERTUSI, Chem. Abstracts 25, 2076 (1931).

as 40 γ fluoride in 10 ml. Miller[229b] reports that this compound can serve as the weighing form in the gravimetric determination of fluorine.   This material is undoubtedly a complex compound, but its structure has not yet been determined.   One of the following is probably valid:
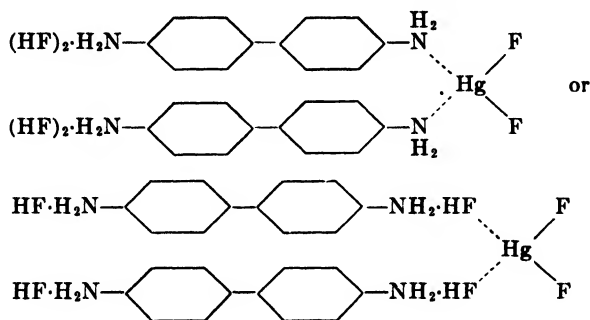
It would be very desirable to have this matter cleared up, as no other complex compounds of this architecture have been previously reported, and it may be that this special type of binding is responsible for the specificity of the fluoride precipitation.

It would be interesting, from the viewpoint of ascribing the analytical effects of organic reagents to certain atomic groupings, to make compara-tive studies of the behavior of the homologs of benzidine toward sulfuric and tungstic acid.   Such ·homologs are all diphenyldiamines with the NH_2 groups in positions other than 4,4'.   The only available observation along this line was made by Feigl and Willfort.[230]   They found that 4,2'-diaminodiphenyl (I), which is sometimes called "diphenyline," is an excellent quantitative precipitant for tungstic acid, whereas it has no precipitating action toward sulfuric acid.   Accordingly, it appears that the particular location and steric position of both NH_2 groups, as they are situated in benzidine, is significant for the production of insoluble sulfates.   In harmony with this is the fact that, of the two isomeric diaminofluorenes, only the 2,7 isomer (II) forms a sulfate precipitate, while the 2,5 isomer (III) does not.[231]
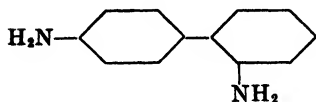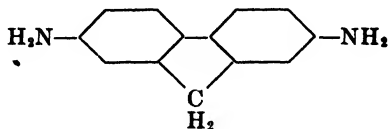
[229b] C. F. MILLER, *Chemist-Analyst* **26**, 35 (1937).
[230] Compare F. FEIGL, *Rec. trav. chim.* **58**, 471 (1939).
[231] J. SCHMIDT and W. HINDERER, *Ber.* **65**, 65, 87 (1932).
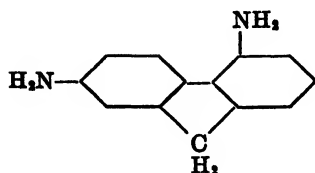
(III)

Nothing has been reported concerning the behavior of (II) and (III) toward tungstic acid. Reasoning from the similar behavior of benzidine and diphenyline hydrochloride toward alkali tungstate, it can be anticipated that the two diaminofluorenes will be quantitative precipitants for tungstic acid, and that the 2,5-isomer will even function selectively. The divergent actions of benzidine and diphenyline toward sulfuric and tungstic acid indicate that the precipitates do not have analogous constitutions. With respect to the tungstate precipitation, it is probably not a matter of the diacidity of the benzidine base, but rather that the activity one NH$_2$ group is adequate. Supporting evidence is provided by the fact that the hydrochlorides of numerous monoacidic organic bases behave in an analogous manner to benzidine hydrochloride toward alkali tungstate.[231a]

In this connection, mention should be made of naphthidine. This base is a homolog of benzidine; the phenyl groups are replaced by naphthyl groups, and the NH$_2$ groups are situated in the p, p' positions. Nietzki and Goll[232] report that naphthidine sulfate is even less water-soluble than benzidine sulfate. The weighting effect of the C$_{10}$H$_7$ group may accordingly offer an advantage here, and a study of the quantitative precipitation of tungstate by naphthidine would be especially interesting.

Hovorka[232a] made interesting studies of the analytical behavior of the condensation products of benzidine with aromatic aldehydes. Under proper conditions, this condensation involves only one of the two NH$_2$ groups of benzidine and leads to the colored materials known as Schiff's bases. They are quite soluble in acetic acid and also in alcohol. The color of these bases is retained in their precipitation products. Thus, vanillylidenebenzidine, HO(CH$_3$)C$_6$H$_3$—CH=N—C$_6$H$_4$—C$_6$H$_4$—NH$_2$, produces a red-brown precipitate with acidified tungstate solutions. This adsorption compound contains all of the tungstic acid, and hence the latter can be quantitatively precipitated in this way. However, molybdates act in the same fashion and so the selective precipitating action of

[231a] See J. H. Yoe and L. A. Sarver, op. cit., p. 206.

[232] R. Nietzki and O. Goll, Ber. 18, 3255 (1885).

[232a] V. Hovorka, Chem. Abstracts 33, 1624, 6194 (1939).

benzidine toward tungsten seems to have been lost in the benzidine derivatives prepared by Hovorka.

The salts of benzidine and other organic nitrogen bases with acids are often regarded as principal valence compounds.in analogy to ammonium salts, whose organic derivatives they are, in fact. It is thus assumed that there is a valence change of the nitrogen from 3 to 5 when the salt is formed. On the other hand, as was pointed out in Chapter III, Werner viewed ammonium salts as coordination compounds between NH_3 molecules and H^+ ions of acids. The difference in these two ways of viewing ammonium salts is shown in the formulas:

$$[H_3N....H^+]X^-$$

Analogously, benzidine sulfate can be represented by a principal valence formula (I) and a coordination formula (II):

(I)

(II)
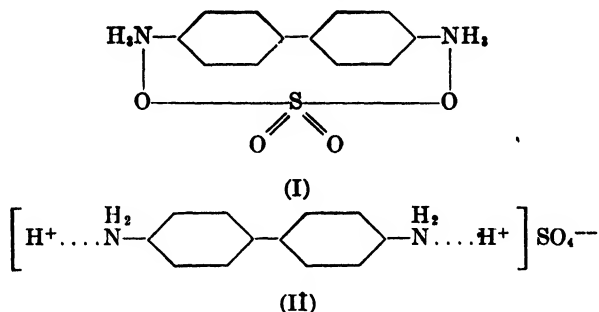
A comparison of (I) and (II) plainly reveals the superiority of the coordination chemical viewpoint. Formula (I) shows a ring closure, which is open to serious question, both with respect to the number of ring members and from steric considerations. On the other hand, (II) presents a picture that agrees exactly with the findings obtained from the X-ray study of electrolytes, namely, that their cations and anions exist not merely in solution but also constitute separate structural elements in the solid substance.

The foregoing consideration shows that a principal valence formula [analogous to (I)], can be replaced by a coordination formula [analogous to (II)] in representing salts of benzidine with acids, in which benzidine functions as cation. Things are different with regard to certain complex metal salts, which contain benzidine (Bzdn) as neutral portion. The compounds $PdCl_2 \cdot Bzdn$ and $PdBr_2 \cdot Bzdn$ have been known for a

long time.[232a] They are quite similar to the ammoniates $PdCl_2 \cdot 2NH_3$ and $PdBr_2 \cdot 2NH_3$, and it seems logical to assume that a molecule of benzidine occupies two coordination positions on the palladium atom in exactly the same manner as two ammonia molecules. Spacu[232b] has isolated a large number of weakly soluble complex compounds of metal salts with benzidine, which show the following compositions:

| X = one acid equivalent | $Me^{II}X_2 \cdot 1Bzdn$ $Me^{II} = $ Co, Cu, Ni, Hg | $Me^{IIa}X_2 \cdot 2Bzdn$ $Me^{IIa} = $ Zn, Ni | $Me^{III}X_3 \cdot 3Bzdn$ $Me^{III} = $ Al, Fe, Cr |

All known benzidine compounds with metal salts correspond to well.known ammoniates and ethylenediamine compounds of metal salts, in which one molecule of benzidine has taken the place of each two molecules of ammonia or of one molecule of ethylenediamine. The corresponding coordination formulas of the compounds of the type $Me^{II}X_2 \cdot 1Bzdn$ should accordingly be written as shown in (III). The assumption that the compounds $Me^{II}X_2 \cdot Bzdn$ in the bimolecular form produce complex compounds, would lead to the binuclear coordination formula (IV):
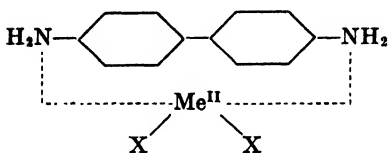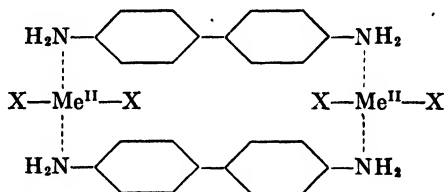
(III)   (IV)

Both (III) and (IV) present multi-membered chelate compounds, which are in contradiction to all previous experience concerning maximal ring numbers in complex compounds. Of course, (IV) as a binuclear compound might be expected to occupy an exceptional position. Formulas analogous to (IV) could be written for the other benzidine complex salts just cited. On the other hand, it seems very unlikely that the very symmetrically constructed benzidine will enter into coordinative binding with only one of its NH_2 groups. Hence, the constitution of the Spacu compounds has not been definitely decided. Perhaps exceptional cases, namely, multinuclear complex compounds, may make it necessary to take into account the formation of extreme polymembered chelate compounds. The complex compounds of fuchsine with $AuCl_3$ and $PdCl_2$ studied by West (see p. 310) indicate this possibility.

The benzidine compounds of metal salts have not been brought into

[232a] A. GUTBIER, A. KRELL, and R. L. JANSSEN, Z. anorg. allgem. Chem. **47,** 36 (1906).

[232b] G. SPACU, Chem. Abstracts **19,** 2944 (1925).

this discussion merely to raise the question of the difficulty of assigning to them a correct formulation. The compounds $Cu(CNS)_2 \cdot Bzdn$ and their analogous tolidine compounds are formed with ease. They are so slightly soluble that they have been recommended as selective forms for the precipitation of copper.[232c]

The Selective Action of α,α'-Dipyridyl and α,α'-Phenanthroline and their Ferrous Compounds

Blau,[233] in a classic paper on complexes, showed that α,α'-dipyridyl (I), α,α'-phenanthroline (II), and α,α'-dipiperidyl (III),
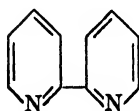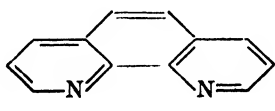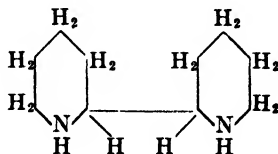
(I) (α,α'-dip)   (II) (α,α' phen)   (III)

form water-soluble intensely red ferrous salts, that are stable toward acids. These salts produce colored complex ions, such as $[Fe(\alpha,\alpha'\text{-dip})_3]^{++}$ and $[Fe(\alpha,\alpha'\text{-phen})_3]^{++}$:
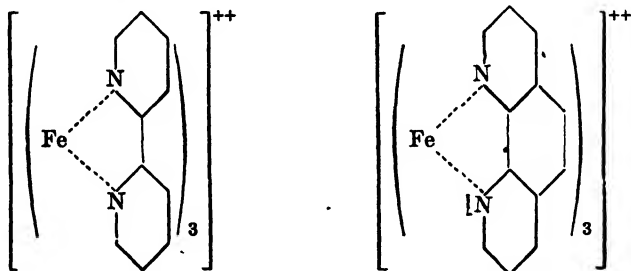
The complex ions are of the hexammine type, since six coordination positions of the iron atom are occupied by three molecules of base, each containing two nitrogen atoms. In contrast to most ferrous salts, which readily undergo autooxidation, the complex compounds containing these bases are extraordinarily stable, and quite resistant to even alkalies and alkali sulfides. This stability obviously is due to the five-membered rings in the complex ions. It is characteristic of the firm linking of the nitrogen-containing auxiliary valence rings, that the valence isomeric ferridipyridyl ion or ferriphenanthroline ion cannot be prepared, for instance, from ferric salts and the corresponding bases. They are

[232c] G. Spacu and G. Marcarovici, Z. anal Chem. 102, 350 (1935). See also Z. Karaoglonov, ibid. 119, 16 (1940).

[233] F. Blau, Monatsh. 19, 647 (1898).

formed only by direct oxidation, by means of permanganate in acid solution, of ferrodipyridyl ion or ferrophenanthroline ion; once formed, they can be reconverted into the ferro compounds by even the weakest reducing agents. Consequently, the dipyridyl and phenanthroline compounds present a complete reversal of the stability relationships usually displayed by soluble non-complex ferrous salts. It is significant, in view of the recent pronounced trend toward making extensive use of organic reagents in analytical chemistry, that the precise statements of Blau concerning the reaction capabilities of α,α'-dipyridyl and α,α'-phenanthroline were given no attention until thirty years later with respect to applying these compounds as specific reagents for the detection and quantitative (colorimetric) determination of ferrous salts. Such belated recommendations were made simultaneously, but independently, by Hill[244] and Feigl and Hamburg.[235] Shortly thereafter, Walden, Hammett and Chapman[236] suggested ferrous phenanthroline sulfate as a redox indicator for titrations with permanganate, dichromate, and ceric sulfate. As just stated, this compound can be oxidized, in acid solutions, to blue ferriphenanthroline sulfate.

Morgan and Burstall[237] found that α,α',α''-tripyridyl (IV) likewise reacts with ferrous ions to form a red hexammine ion (IV*). The coordination formula shows that two molecules of tripyridyl have been coordinated in
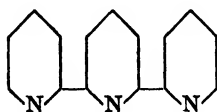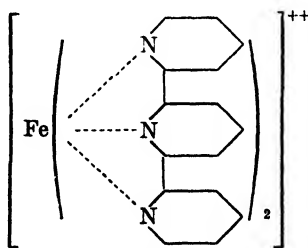
(IV)   (IV*)

this complex ion. The behavior of (I) to (IV) leaves no doubt that the

or
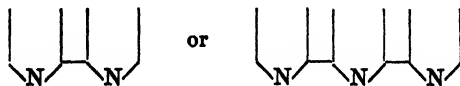
[244] R. Hill, *Proc. Roy. Soc. (London)* **107**, 205 (1930), *Chem. Abstracts* **25**, 2387 (1931).

[235] F. Feigl and H. Hamburg, *Z. anal. Chem.* **86**, 1 (1931); see also *ibid.* **93**, 199 (1932).

[236] G. H. Walden, L. P. Hammett and R. P. Chapman, *J. Am. Chem. Soc.* **53**, 3908 (1931); **55**, 2649 (1933).

[237] G. Morgan and F. Burstall, *J. Chem. Soc.* **135**, 20 (1932).

groups are the determining factors for the formation of the red inner complex ferro- ions and hence for the specificity of the iron reaction.   Consequently, the behavior of derivatives of α,α'-dipyridyl are worthy of attention with respect to the effect on the action of this group.   Compounds V to IX were studied by Smirnoff,[288] and by Willink and Wibaut.[289]

(V)   (VI)   (VII)

(VIII)   (IX)
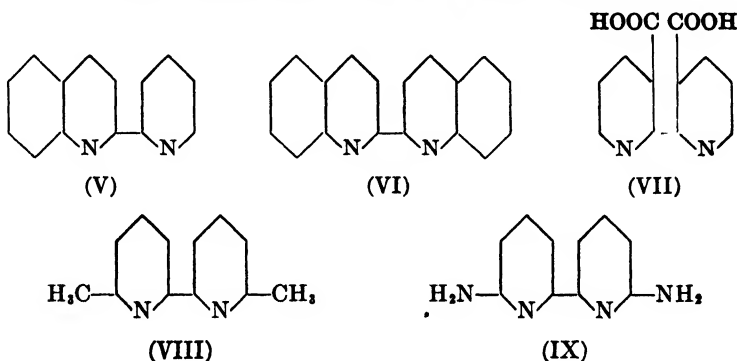
Contrary to expectation, these derivatives of dipyridyl do not react with ferrous salts.   The divergent behavior of (V) and (VI), according to Smirnoff, is explained plausibly by assuming that an inner molecular coordinative claim on the nitrogen is made by the system of conjugated double bonds adjacent to one or two nitrogen atoms.   This assumption is in agreement with the relative behavior of pyridine and quinoline. The latter has a lower basicity and also a smaller addition capacity than pyridine, a finding which obviously can be ascribed to the fact that the auxiliary valence activity in quinoline is interfered with by the steric proximity of the conjugated double bonds of the benzene ring, whereas in pyridine, which is completely symmetrical, there is no such interference. Such considerations, however, are not valid for the compounds (VII) to (IX).   A uniform and plausible explanation for the nonreactivity of (VII) to (IX) is that the molecular volume of the bases is too great to allow space for coordination on an iron atom (compare p. 425).

The different behavior of the foregoing compounds toward ferrous salts, therefore, shows clearly that there are circumstances in which a negative influence of substituents must be taken into account even though a specific group is known to be present in the molecule of an organic reagent.

The favoring of the ferro- state in stable coordination compounds with α,α'-dipyridyl and phenanthroline is remarkable because two other compounds quite similar to α,α'-dipyridyl, namely, α-(α'-pyridyl)-

[288] A. Smirnoff, *Helv. Chim. Acta* 4, 802 (1921).
[289] H. Tjeenk Willink, Jr., and J. Wibaut, *Rec. trav. chim.* 54, 275 (1935).

pyrrole (I) and α-pyridylhydrazine (II),
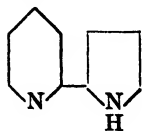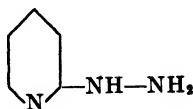
(I)   (II)

also form complex iron^{II} salts or ions, namely[240]
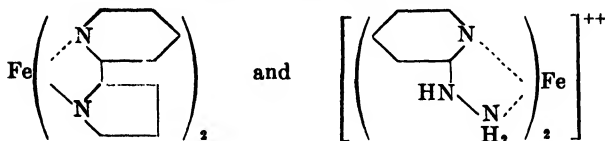
However, in contrast to the Blau compounds, these are very unstable, and by oxidation in the air immediately go over into the corresponding ferri- salt.

The production of complex red [Fe(α,α'-dip)$_3$]$^{++}$ and [Fe(α,α'-phen)$_3$]$^{++}$ ions, in mineral acid solution, by coordination of dipyridyl and phenanthroline molecules on the Fe^{++} ion, is the most striking action of these two bases. The coordination capability is not limited to the iron atom, and therefore is not specific. Blau himself (*loc. cit.*) observed that Cu^{++}, Cd^{++}, and Zn^{++} ions also add dipyridyl and phenanthroline in acid solutions, with production of ammine ions. Of these, only [Cu(α,α'-dip)$_2$]$^{++}$ and [Cu(α,α'-phen)$_2$]$^{++}$ ions are light blue. Accordingly, it is possible to detect ferrous iron directly, provided not too much copper is present.[241] On the other hand, molybdenum at lower valences also produces a water-soluble red compound with α,α'-dipyridyl.[242] The composition of this product has not been established.

Tartarini[243] observed another remarkable specific action of α,α'-dipyridyl and α,α'-phenanthroline. If cuprous iodide or thiocyanate is precipitated in the presence of one of these bases, intensely colored addition compounds are produced. The writer has found that these products

[240] B. EMMERT and co-workers, *Ber.* **60**, 2211 (1927); **62**, 1733 (1929); **66**, 1871 (1933).

[241] M. L. Moss and M. G. MELLON [*Ind. Eng. Chem., Anal. Ed.* **14**, 862 (1942)] found that α,α',α''-tripyridyl forms intensely colored ammine ions with Cu^{++}, Co^{++} and Ni^{++} ions. However, it is not known definitely whether the intense color is due to the coordination of two moles of tripyridyl on these cations. It is also possible that the complex equilibrium [Me(α,α',α'')$_2$]$^{++}$ $\rightleftharpoons$ Me^{+++} + 2α,α',α'' lies farther to the left than the equilibrium [Me(α,α')$_3$]$^{++}$ $\rightleftharpoons$ Me^{++} + 3α,α' of the corresponding dipyridyl compounds.

[242] A. KOMAROWSKY and N. S. POLUEKTOFF, *Mikrochim, Acta* **1**, 264 (1937).

[243] G. TARTARINI, *Gazz. chim. ital.* **63**, 597 (1933).

also result if the dry colorless cuprous halides are digested with alcoholic solutions of the bases. The following salts were isolated by Tartarini:

$CuCNS \cdot \alpha,\alpha'$-dip............. orange $CuCNS \cdot \alpha,\alpha'$-phen..... yellow brown
$CuI \cdot \alpha,\alpha'$-dip............... red $CuI \cdot 2\alpha,\alpha'$-phen........ dark blue

These complexes are decomposed into their components on treatment with acids. Consequently, they are probably addition compounds, in contrast to the ferrous compounds, which are intercalation compounds. Formula (I) or the bimolecular formulas (II) or (III)[244] can be written to show the coordination structure of the colored cuprous complexes

$$\alpha{-}{-}{-}\alpha' \qquad \alpha{-}{-}{-}\alpha' \quad \alpha{-}{-}{-}\alpha' \qquad\qquad \alpha{-}\alpha'$$

$$\text{Cu} \qquad\qquad \text{Cu}{-}{-}{-}\text{Cu} \qquad\qquad \text{Hal}{-}\text{Cu}{-}{-}{-}\text{Cu}{-}\text{Hal}$$

$$\mid \qquad\qquad\qquad \mid \qquad \mid \qquad\qquad\qquad\qquad \alpha{-}\alpha'$$

$$\text{Hal} \qquad\qquad\qquad \text{Hal} \quad \text{Hal}$$

$$\text{(I)} \qquad\qquad\qquad \text{(II)} \qquad\qquad\qquad\qquad \text{(III)}$$
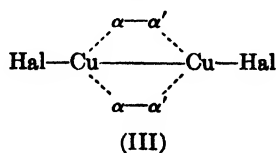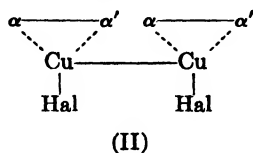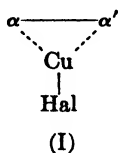
$\alpha{-}\alpha' = \alpha,\alpha'$-dipyridyl or α,α'-phenanthroline

Hal = I, CNS

These copper compounds exhibit clearly the effect of the coordination of the base molecules that is also shown in the iron compounds. However, while the coordination of either of the bases on the iron atom produces complex ions of the same color, the cuprous compounds are of different colors. This fact, along with the instability toward acids, indicates that the compounds are constructed differently. Other slightly soluble metal halides have no tendency to coordinate with dipyridyl and phenanthroline. Hence, this action of these two bases is specific, and can be used to identify dry cuprous halides.

Only water-soluble ferrous α,α'-dipyridyl and α,α'-phenanthroline salts were originally used for the detection and colorimetric determination of iron, and as indicators in redox reactions. Feigl and Miranda[245] showed that certain slightly soluble compounds of ferrous dipyridyl and phenanthroline also have analytical utility. Such salts are formed when $[Fe(\alpha,\alpha'\text{-dip})_3]^{++}$ or $[Fe(\alpha,\alpha'\text{-phen})_3]^{++}$ cations meet anions with large volumes. The following ions, acids, and complex acido ions can be precipitated in this way, some of them even quantitatively: MoO_4^{--} WO_4^{--}, IO_3^-, $H_3PO_4 \cdot 12MoO_3 \cdot$ aq, $H_3PO_4 \cdot 12WO_3$ aq, picric acid, aurin tricarboxylic acid, $[BiI_4]^-$, $[HgI_4]^{--}$, $[CdI_4]^{-}$, $[Ni(CN)_4]^{--}$, $[Co(CN)_6]^{---}$, $[Zn(CN)_4]^{--}$, $[Cd(CN)_4]^{--}$, $[Hg(CNS)_4]^{--}$, etc., also $H[AuCl_4]$, $H_2[PtCl_6]$,

[244] In coordination formulas (II) and (III) the copper atom has the coordination number = 4, which is more likely than the coordination number = 3 in (I). A decision as to which formulation is correct may possibly be reached from a study of the behavior of α,α',α''-tripridyl toward cuprous halides.

[245] F, Feigl and L. I. Miranda, *Ind. Eng. Chem., Anal. Ed.* **16**, 141 (1944).

$H_2[PdCl_4]$, as well as the corresponding bromine and iodine compounds. All the precipitates produced by the union of $[Fe(\alpha,\alpha'\text{-dip})_3]^{++}$ or $[Fe(\alpha,\alpha'\text{-phen})_3]^{++}$ with the foregoing compounds or ions are crystalline. The colors of these products range from red, red-violet, to blackish red. This observation indicates that the red complex iron ions constitute the chromotropic constituent of the respective slightly soluble salts. It seems probable that these complex iron ions may function as general precipitants for voluminous anions, and particularly for complex anions. The quantitative precipitability of cadmium as $[Fe(\alpha,\alpha'\text{-dip})_3][CdI_4]$, after conversion of Cd^{++} into $[CdI_4]^{--}$, is worthy of special attention. It provides not only a very selective spot test for cadmium, but, in fact, is the most sensitive test known for this metal. The identification limit is 0.05γ Cd, at a concentration limit of $1:1,000,000$.[246]

The quantitative precipitation of gallotannin, from an ammoniacal solution, by $[Fe(\alpha,\alpha'\text{-dip})_3]^{++}$ and $[Fe(\alpha,\alpha'\text{(phen)}_3]^{++}$ ions is interesting. The flocculent violet precipitate is not soluble in acetic acid. Its composition has not been established. Since gallotannin may form insoluble adsorption compounds (compare Chapter X) with many metals it is likely that the precipitate is an adsorption compound containing tannin or its oxidation products, along with $[Fe(\alpha,\alpha'\text{-dip})_3](OH)_2$ or $[Fe(\alpha,\alpha'\text{-phen})_3](OH)_2$. Other vegetable tanning agents show a similar behavior toward these reagents, and thus sensitive tests for tannins can probably be developed.[247] Synthetic tanning agents remain unaltered, and perhaps a method of distinguishing them from natural materials may be developed on the basis of this behavior.

Red precipitates are formed by the addition of $[Fe(\alpha,\alpha'\text{-dip})_3]^{++}$ or $[Fe(\alpha,\alpha'\text{-phen})_3]^{++}$ ions to ammoniacal solutions of Congo red and benzopurpurine, which are typical semicolloids. Hence, future studies may show that these complex ions can function as precipitants for other organic emulsoids and semicolloids that exhibit acid character.

Uncompleted studies have shown that solutions of the hydrochlorides of α,α'-dipyridyl and α,α'-phenanthroline also act directly as precipitants toward solutions of the halogenato acids of gold, platinum, and palladium.[248] The test solutions contained 1% of the metal; 1 ml. portions were taken in each trial. The results were:

$H[AuCl_4]$	$H_2[PtCl_6]$	$H_2[PdCl_4]$
white	yellow	white-yellow
$H[AuBr_4]$	$H_2[PtBr_6]$	$H_2[PdBr_4]$
red-brown	orange-red	yellow-brown
$H[AuI_4]$	$H_2[PtI_6]$	$H_2[PdI_4]$
brown-black	blue-black	brown-red

[246] F. FEIGL, Spot Tests, p. 74.

[247] F. FEIGL and H. E. FEIGL, *Ind. Eng. Chem., Anal. Ed.* **18**, 62 (1946).

[248] F. FEIGL, L. I. MIRANDA and H. A. SUTER, unpublished studies.

There obviously is a distinct relationship between the color of the precipitation product and the atomic weight of the halogen of the halogenato acids. The color deepens in the order Cl-Br-I. The solubility in water shows a similar weighting effect; it decreases from Cl to I.

The analytical data indicate that the precipitates, in the case of gold and platinum, are salts of the organic diacidic bases with the respective halogenato acids. This agrees with the fact that $H[AuCl_4]$ and $H_2[PtCl_6]$ are precipitants, through salt-formation, for high atomic organic bases, such as the alkaloids. On the other hand, the palladium halogenato acids behave differently. With α,α'-dipyridyl they form compounds of the $PdX_2 \cdot \alpha,\alpha'$-dip type. $PdCl_2 \cdot \alpha,\alpha'$-dip was produced by precipitating $H_2[PdCl_4]$ with α,α'-dipyridylhydrochloride, or by digesting anhydrous $PdCl_2$ with an alcoholic solution of α,α'-dipyridyl. The addition compounds of PdX_2 and α,α'-dipyridyl patently are analogs of the addition compounds of cuprous halides with α,α'-dipyridyl or α,α'-phenanthroline (see p. 323). It is noteworthy, and also indicative of the great stability with which α,α'-dipyridyl (or α,α'-phenanthroline) is fixed on $PdCl_2$, that a solution of $H_2[PdCl_4]$ or $Na_2[PdCl_4]$ on treatment with $[Fe(\alpha,\alpha'-dip)_3]SO_4$ produces first a red precipitate which is obviously $[Fe(\alpha,\alpha'-dip)_3][PdCl_4]$. At room temperature, this gradually transforms into white-yellow $PdCl_2 \cdot \alpha,\alpha'$-dip. This change, which occurs rapidly on warming, also proceeds in a solution that contains large amounts of NaCl. In the latter case, the normal feeble dissociation $Na_2[PdCl_4]$ $\rightleftharpoons PdCl_2 + 2NaCl$, is still less pronounced. Therefore, it is quite possible that the initial products of the action of these bases on palladium halogenato acids are unstable salts of the acids. These salts then transform into addition compounds of the palladous halide:

$$H_2[PdX_4] + \alpha,\alpha'\text{-dip} \rightarrow \alpha,\alpha'\text{-dip} \cdot H_2[PdX_4] \tag{1}$$
$$\alpha,\alpha'\text{-dip} \cdot H_2[PdX_4] \rightarrow PdX_2 \cdot \alpha,\alpha'\text{-dip} + 2HX \tag{2}$$
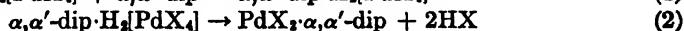
The change shown in (2) would be an interesting inner-molecular shift of α,α'-dipyridyl. In principle, it is analogous to the transformation, just discussed, of $[Fe(\alpha,\alpha'-dip)_3][PdCl_4]$ into $PdCl_2 \cdot \alpha,\alpha'$-dip.

The findings cited in this section show that the selective activity of α,α'-dipyridyl and α,α'-phenanthroline can be classified under the following different types of reaction:

(1) Addition of the bases to Fe^{++} ions, with formation of stable, red $[Fe(\alpha,\alpha'-dip)_3]^{++}$ or $[Fe(\alpha,\alpha'-phen)_3]^{++}$ complex ions.

(2) Precipitating action of the complex ions [see (1)] toward voluminous and complex anions, and toward acid emulsoids and semicolloids.

(3) Addition of the bases to cuprous and palladous halides, with formation of water-insoluble addition compounds, usually colored.

(4) Precipitating action toward gold and platinum halogenato acids with production of heteropolar salts.

Up to the present, only the reactions given in (1) and (2) have been used in analytical practice. However, it is entirely possible that reaction types (3) and (4) may prove useful in analysis. There has been no study of these possibilities, nor of the behavior of the salts of other platinum metals toward α,α'-dipyridyl and α,α'-phenanthroline.

Selective Activity of the p—ON—C_6H_4—N< Group

Yoe and Overholser[249] found that the light yellow alcoholic solutions of p-nitrosophenylamines such as p-nitrosoaniline (I), p-nitrosodimethylaniline (II), p-nitrosodiethylaniline (III) and p-nitrosodiphenylamine (IV)

ON—⟨ ⟩—NH₂

(I)

ON—⟨ ⟩—N(C₂H₅)₂

(III)

ON—⟨ ⟩—N(CH₃)₂

(II)

ON—⟨ ⟩—N(H)—⟨ ⟩
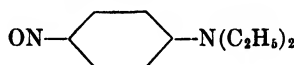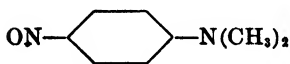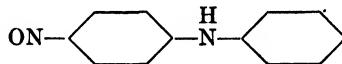
(IV)

react with palladium salts in neutral or weakly acid solutions (pH = 5–6) to form colored precipitates. These products can be considered as molecular compounds:
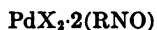
$$PdX_2 \cdot 2(RNO) \qquad X = \text{univalent acid radical}$$
$$RNO = \text{(I) to (IV)}$$

The palladium compound of (I) is dark brown; those of (II) and (III) light red; that of (IV) dark purple-brown. The intense color is to be attributed to a chromotropic effect or some other influence of the NO-group, since aniline, dimethylaniline, and p-substituted anilines do not produce colored compounds when added to palladous chloride solution.

Palladium salts of the general formula just given and containing molecules of p-nitrosophenylamines as neutral parts should more probably be formulated as addition compounds, $PdX_2 \cdot 2RNO$, rather than as the isomeric intercalation compounds $[Pd(RNO)_2]X_2$. This is demonstrated by the fact that white palladium cyanide, which is not soluble, reacts with alcoholic solutions of p-nitrosoamines in the same manner as soluble palladium salts.[250] It is not definitely known whether the binding of the two base molecules in the addition compounds is effected by the nitrogen atom of the amino group or by the oxygen or

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[249] J. H. Yoe and L. G. Overholser, *J. Am. Chem. Soc.* **61**, 2058 (1939); **63**, 3224 (1941).

[250] F. Feigl, unpublished observations.

nitrogen atom of the nitroso group.   In other words, any of the following is possible:

$$\underset{X}{\overset{X}{ON-C_6H_4-\underset{|}{\overset{|}{N}}...\overset{|}{Pd}...\underset{|}{\overset{|}{N}}-C_6H_4-NO}} \quad \text{or} \quad N-C_6H_4-NO...\overset{X}{\underset{X}{Pd}}...ON-C_6H_4-N$$

$$\text{or} \quad N-C_6H_4-\overset{O}{N}...\overset{X}{\underset{X}{Pd}}...\overset{O}{N}-C_6H_4-N$$
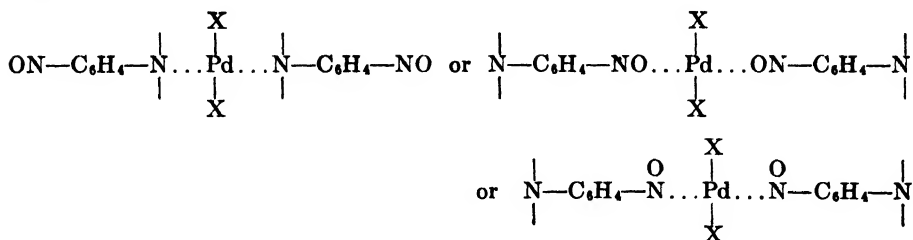
The binding of the base molecules by the nitrogen atom of the amino group corresponds to the ability of the palladous chloride to add molecules of ammonia, aniline, and p-nitrosoaniline.[251]   On the other hand, the possibility of coordination by the NO-group of the base molecule should not be rejected, in view of the existence of colored addition compounds between nitrosoaniline and phenols and amines.[252]

The behavior of p-nitrosophenylamines toward palladous ions can be considered as a selective action of the p-ON—C_6H_4—N< group because, in addition to palladium ions, only Au, Ag, and Pt ions form colored compounds with the nitrosoamines (I) to (IV).   The precipitation sensitivity of the three noble metal ions is, however, far lower than that of palladium ion.   Yoe and Overholser could, therefore, not only recommend p-nitrosoamines (especially the dimethyl- and diethylaniline compounds) as sensitive and selective reagents for palladium (0.005γ/drop) but, with the aid of these reagents, they also carried out satisfactory colorimetric determinations of small amounts of palladium.

It is not possible to make use of the invitingly low palladium content of the nitrosophenylamine compounds for gravimetric determinations of this metal.   The precipitates adhere tenaciously to glass and are difficult to filter.   Furthermore,when dried at 110°C., they give up their moisture but slowly, and they gradually decompose at temperatures above 120°C.   This behavior strikingly demonstrates that the great advantages that come from the selectivity and sensitivity of reactions cannot always be utilized because of effects that only come to light when the reactions are tried in actual practice.

Preliminary unpublished studies by the author indicate that the palladium reaction can probably be used for the detection of small

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[251] A. GUTBIER and co-workers, *Ber.* **39**, 1292 (1906); *Z. anorg. allgem. Chem.* **95**, 129 (1921).

[252] Compare H. TORREY and C. GIBSON, *J. Am. Chem. Soc.* **35**, 246 (1906); also R. KREMANN, *Monatsh.* **25**, 1311 (1904); **40**, 63 (1919).

amounts of *p*-nitroso aromatic amines. Furthermore, it seems to be possible to detect tertiary aromatic amines (with free *p*-positions) by this reaction, since their nitrosation by means of nitrous acid proceeds easily. Definite studies of these tests have not been made.

The Silver-Binding NH— *Group*

Numerous organic compounds containing an NH— group react in water solution with silver, cuprous, or mercury salts to form insoluble compounds. The imide hydrogen is replaced by an equivalent of the metal. Analogous compounds with other metals are much less frequent and can never be prepared so simply. This selective action of the NH— group obviously is due to an especially strong union between the nitrogen and the silver or mercury.[253] Consequently, silver-binding reagents should be sought among those organic compounds that have an NH group, and all the more so because their silver derivatives frequently are insoluble in even ammonia or acids. This is an important point for analytical purposes.

p-Dimethylaminobenzylidenerhodanine has proved a useful reagent for silver. Besides its selective action it has the added advantage of an extraordinary sensitivity. It is a derivative of the easily accessible rhodanine, that can be used as a starting point for studying the far-reaching independence of a selective group action. Several investigations along this line[254] are discussed here because they also are of interest with respect to the experimental proof of a characteristic group action.

Rhodanine
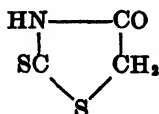
forms whitish-yellow precipitates in dilute nitric acid solution on treatment with silver or mercury salts. The silver compound corresponds exactly to the formula for the silver salt of rhodanine; with mercury, sulfo salts seem to be produced in addition to the salt of rhodanine. With the exception of gold, platinum, palladium,[255] and cuprous salts, which usually resemble the silver salts in their reactions, other metal salts

---

[253] Palladium and nitrogen seem to have great affinity for each other. This is revealed by the frequency and ease with which N-containing compounds produce principal and auxiliary compounds with palladium. Consequently, when considering the activity of acidic NH groups, it is necessary to keep in mind not only the formation of silver salts but also those of palladium.

[254] N. URMANN, Dissertation, Vienna, 1928; H. Pollak, Dissertation, Vienna, 1928.

[255] Experiments with E. Rajmann have shown the existence of an addition compound of PdCl₂ and rhodanine.

produce no precipitates with rhodanine in nitric acid solution. Accordingly, rhodanine in acid solution exhibits a considerable selectivity. This characteristic is lost if the reaction is carried out in alkaline solution, because almost all metal salts then give precipitates containing rhodanine. The products partially decompose, more or less rapidly, and form sulfides. The different behavior of rhodanine in acid and alkaline media indicates either an alteration in the stability of the salts toward H^+ ions or, more probably, a different constitution and a consequently different activity of the rhodanine. Enolizable compounds, in alkaline solution, are often stabilized in the tautomeric enol forms by the formation of alkali salts. In rhodanine, the parent form (I) through the shifting of one H can give rise to the tautomeric enol or sulfhydryl forms (II) to (IV):

$$
\begin{array}{cccc}
\text{HN——CO} & \text{HN——COH} & \text{N═══COH} & \text{N——CO} \\
\text{SC} \quad \text{CH}_2 & \text{SC} \quad \text{CH} & \text{SC} \quad \text{CH}_2 & \text{HSC} \quad \text{CH}_2 \\
\text{S} & \text{S} & \text{S} & \text{S} \\
\text{(I)} & \text{(II)} & \text{(III)} & \text{(IV)}
\end{array}
$$
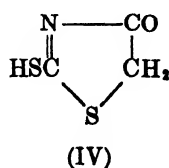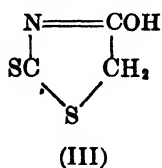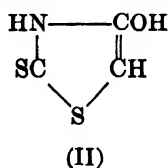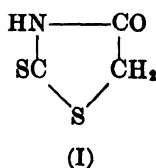
Accordingly, the ability of rhodanine to form a silver salt is due either to the fact that, in acid solution, the equilibrium between (I) and (II) to (IV) lies so far toward (I) that only the silver-binding NH group is active, or even in acid solution the concentration of the forms that contain the salt-forming OH or SH group is still sufficient to permit the attainment of the solubility product of the silver salt. A decision between these alternatives can be reached by altering the rhodanine molecule by stepwise substitution, in such manner that the separate enolization possibilities are removed. Enolization leading to compounds of type (II) is impossible with derivates of rhodanine of the general structure

$$
\begin{array}{l}
\text{HN——CO} \\
\text{SC} \quad \text{C=CHR} \qquad \text{R} = \text{CH}_3, \text{C}_6\text{H}_5, \text{CH=CH·C}_6\text{H}_5, \text{C}_{10}\text{H}_6\text{OH}, \text{C}_6\text{H}_4\text{NH}_2, \text{NOH} \\
\text{S}
\end{array}
$$
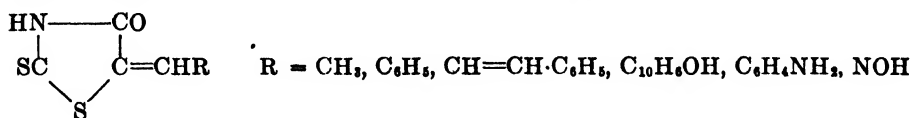
These compounds behave like the parent rhodanine with respect to the production of insoluble precipitates. The same holds for derivatives that have the general structure

$$
\begin{array}{l}
\text{HN——CO} \\
\text{R}_2\text{=C} \quad \text{C=CHR}_1 \qquad
\begin{array}{l}
\text{R}_1 = \text{CH}_3, \text{C}_6\text{H}_5, \text{NOH}, etc. \\
\text{R}_2 = \text{C}_6\text{H}_4\text{NH—N=}, \text{C}_6\text{H}_5\text{N=}
\end{array} \\
\text{S}
\end{array}
$$
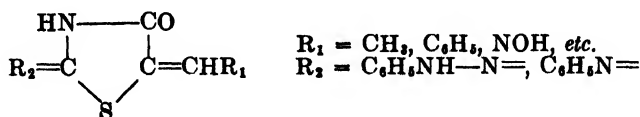
This shows that it is not necessary to assume the existence of the tautomeric forms (II) and (IV) to account for the formation of salts. Finally,

quinrhodine
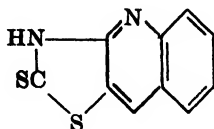
behaves like the parent compound. Hence, an enol form (III) is not essential to the formation of the salt.[256]

A replacement of the sulfur in the CS group of rhodanine by oxygen or hydrogen has a decisive effect on the ability to form insoluble silver salts. Such replacement destroys this precipitating power; on the other hand, the cyclic bound sulfur can be replaced by oxygen with no similar loss of activity.

Rhodanine can be condensed with cyclic compounds, such as cyclohexanone, isatin, quinazolone, and with various sugars, without loss of activity toward silver salts. The condensation of rhodanine with benzaldehydesulfonic acid, for instance (or with glucose), produces quite water-soluble reagents that nevertheless form difficultly-soluble silver salts.[257]

The fact, just pointed out, that a specific group action is retained despite the most varied alteration of the molecule is of special significance from the analytical standpoint, because it provides the possibility of favorably affecting the analytical usefulness of an organic compound by introducing various substituents. These may confer color-forming properties, or they may be groups that promote solubility, or that weight the molecule, or they may provide a combination of all these improvements. In the foregoing instance, the easy condensation of rhodanine with *p*-dimethylaminobenzaldehyde produced *p*-dimethylaminobenzylidene rhodanine
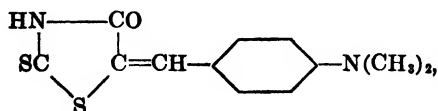
a very sensitive and highly selective reagent for silver. This was the first organic color reagent for silver, and its discovery was the fruit of

[256] Another proof that, in acid solution, the possible equilibria I ⇌ II, I ⇌ III, and I ⇌ IV must greatly favor I is furnished by acetylating rhodanine and then testing the behavior of the product toward phenylhydrazine. If an acetylation in the NH group occurs, it can be expected that a hydrazine radical can be introduced into the intact CO group, while this is impossible in an acetylated enol group. Appropriate experiments have led to crystalline hydrazones, thereby establishing the fact that the hydrogen of the NH group can be replaced by the CH$_3$CO radical.

[257] F. FEIGL and V. ANGER, unpublished studies.

systematic studies having regard for group actions.[258] The significance
of this reagent is demonstrated by the fact that more than 40 publica-
tions on its analytical application have already appeared.

The importance of the CS group adjacent to the NH group in the
formation of the silver salts of rhodanine and its derivatives is clearly
shown by the behavior of 2-thiohydantoin (I), which is similar to rhoda-
nine, and of the condensation products of (I) with p-dimethylamino-
benzaldehyde (II), and with nitrosodiphenylamine (III):
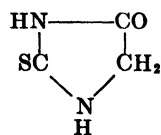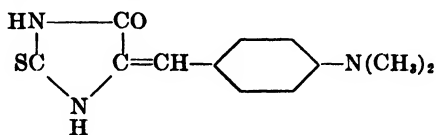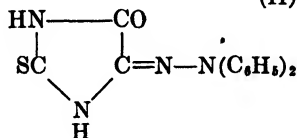
Dubsky[259] found that (I), (II), and (III) form, respectively, violet-rose,
violet, and orange red, slightly soluble silver salts, and also colored
mercury and copper salts.   Furthermore, (III) produces a violet, slightly
soluble lead salt.   He ascribed the reactivity of these compounds toward
copper and lead to the fact that, in addition to the silver-binding group,
$S=C—NH—C=O$, they, in contrast to rhodanine, contain also a second
NH group which enolizes the thioketo group.   This viewpoint is strength-
ened by the finding that these silver salts contain two silver atoms.

Finally, it should be pointed out that Sheppart and Brigham[260] found
that 2-thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine

$$CO—CH_2—NH—CS—NH—CH—CO_2C_2H_5$$
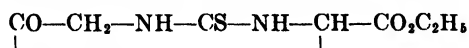
produces a red precipitate with silver salts in acid solution.   The reaction
is even more sensitive than that of silver with p-dimethylaminobenzyl-
idene rhodanine.   This instance also shows that the presence of the
thioketo group is essential for the Ag-specific action of a cyclic NH group.

An interesting example of the silver-binding action of an NH group
adjacent to a CS group (just as in rhodanine) is furnished by dimethyl-
thiopyrimidone (I).   This decidedly basic compound forms very slightly

[258] F. FEIGL, *Z. anal. Chem.* **74**, 380 (1928).

[259] J. V. DUBSKY, *Mikrochemie-Mikrochim. Acta* **28**, 145 (1940).

[260] S. E. SHEPPART and R. H. BRIGHAM, *J. Am. Chem. Soc.* **58**, 1046 (1936).

soluble Ag, Hg, and Pd salts, an observation[261] that can be explained only by the development of an acidic NH group in the tautomeric form (Ia). Condensing (I) at its CH_2 groups with *p*-dimethylaminobenzaldehyde produces bis-dimethylaminostyrylthiopyrimidone (II):

$$
\begin{array}{ccc}
\underset{\text{(I)}}{
\begin{array}{c}
S \\ \parallel \\ C \\
N \diagup \quad \diagdown N \\
CH_3-C \qquad C-CH_3 \\
\diagdown C \diagup \\
H_2
\end{array}}
& \rightleftharpoons &
\underset{\text{(Ia)}}{
\begin{array}{c}
S \\ \parallel \\ C \\
HN \diagup \quad \diagdown N \\
CH_3-C \qquad C-CH_3 \\
\diagdown C \diagup \\
H
\end{array}}
\end{array}
$$

$$
(CH_3)_2N\!\!-\!\!\langle\bigcirc\rangle\!\!-\!\!CH{=}CH-C
\underset{
\begin{array}{c}
S \\ \parallel \\ C \\
N\diagup \;\diagdown N \\
\qquad\qquad C\qquad\qquad \\
C \\ H_2
\end{array}}{}
C-CH{=}CH\!\!-\!\!\langle\bigcirc\rangle\!\!-\!\!N(CH_3)_2
$$

(II)
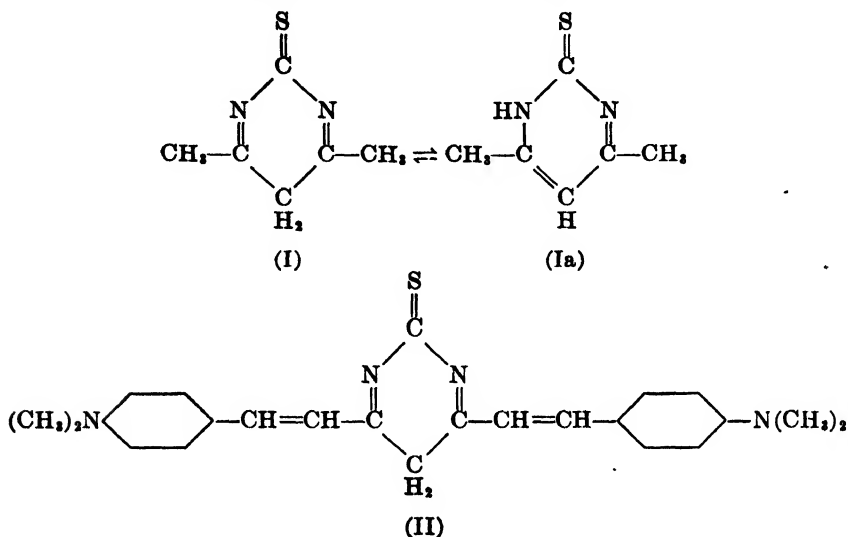
The blue alcohol solution of the sulfate of (II) turns red-brown on the addition of alkalies, obviously because of the formation of the alkali salts of the *aci* form (Ia). It is significant that the Ag, Hg, *etc.*, salts of (II) are also red-brown. Their production permits a very sensitive test for silver and mercury. The mercury salt forms in strong acid solutions even in the presence of large quantities of chloride. Hence, the tendency of this salt to form, and also its stability are exceptional. No other color or precipitation reaction of mercury with organic reagents succeeds under these conditions.

Redox Reactions with Benzidine and Benzidine Homologues

Trillat[262] observed that tetramethyldiaminodiphenylmethane (Arnold's base) is converted into a deep blue oxidation product when treated with lead dioxide or manganese dioxide. This finding, together with a statement by Denigès[263] that lead dioxide produces a blue coloration with benzidine (I), led to the study of the behavior of manganese dioxide toward benzidine. It was found by Feigl and Stern[264] that MnO_2 acts

[261] F. FEIGL and P. KRUMHOLZ, unpublished studies.

[262] A. TRILLAT, *Compt. rend.* **136**, 1205 (1903).

[263] G. DENIGÈS, Precis de chimie analytique, 4th edition, p. 72, 1913.

[264] F. FEIGL and R. STERN, *Z. anal. Chem.* **60**, 24 (1921); compare F. FEIGL, *Chem. Ztg.* **44**, 689 (1920).

similarly to PbO_2, and that benzidine is blued likewise by freshly precipitated $Mn(OH)_2$. The latter, in contact with air, undergoes autooxidation and forms hydrated manganese dioxide: $Mn(OH)_2 + \frac{1}{2}O_2 \rightarrow MnO(OH)_2$. These observations led to experiments designed to develop a new test for manganese. Drops of manganous solution, dilute alkali, and benzidine acetate were placed successively on filter paper; the resulting $MnO_2 \cdot aq$ could thus be revealed by its action on the benzidine. It turned out that this method of forming "benzidine blue" will disclose the presence of as little as 0.15γ Mn in 1 drop (0.05 ml.), which corresponds to 1:330,000. Such minute quantities of manganese could never be detected by observation of the mere formation of $MnO_2 \cdot aq$. It was further demonstrated that manganese can be detected in a solution whose dilution is 1:1,000,000 by a simple modification of the foregoing procedure. A very little calcium chloride is added to the test solution and then a sodium hydroxide solution containing some carbonate. The mixture is warmed and filtered. Any traces of $MnO_2 \cdot aq$ are retained with the $CaCO_3$ and are distinctly revealed when the filter paper is spotted with benzidine. This was one of the first applications of collector action (see Chapters V and XI). These discoveries of spot tests, whose sensitivities seemed astounding at the time (1920–1921), gave rise to the hope that other new tests, based on spot reactions, would be discovered or developed, and that they would be applicable to microanalytical objectives.

Schlenk[265] is principally responsible for the elucidation of the formation of benzidine blue from benzidine. Oxidation of the latter produces a meriquinoid compound, *i.e.*, one molecule of benzidine is oxidized to a *p*-quinoneimide (II), which then unites with a molecule of unchanged benzidine and acid to form a meriquinoid molecular compound. The following· equations represent the production of benzidine blue (III):

(III)

HX = 1 equivalent of acid
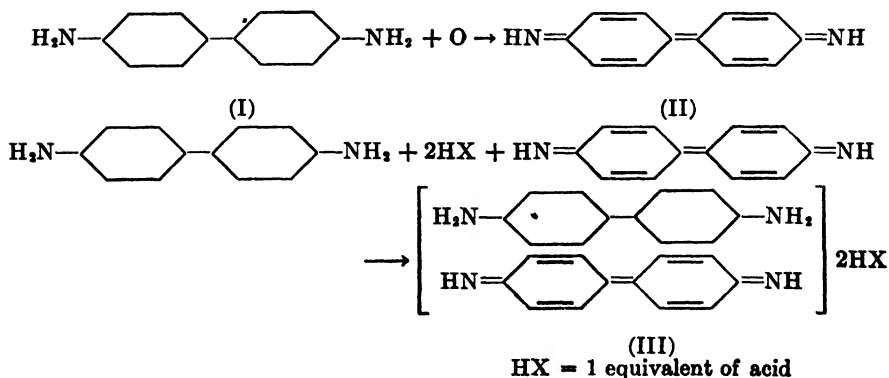
[265] W. Schlenk, *Ann.* **363**, 313 (1908).

The great sensitivity of the benzidine spot test reaction for manganese is not due entirely to the activity of the manganese dioxide produced by autoxidation. A rather important factor is the participation of benzidine in the autoxidation itself. During the latter process, one-half an oxygen molecule is consumed by one molecule of the $Mn(OH)_2$, and thus atomic oxygen is produced (see p. 333). In the absence of benzidine, the atomic oxygen is taken up by a second molecule of $Mn(OH)_2$. However, when benzidine is present, it combines with some of the atomic oxygen and forms benzidine blue. Accordingly, the autoxidation of $Mn(OH)_2$ induces the oxidation of benzidine. If this conception is valid, other autoxidizable materials should be capable of bringing about the production of benzidine blue from benzidine. Feigl[266] proved that cerium can be detected quite similarly to manganese since $Ce(OH)_3$, precipitated by bases, is autoxidized to $CeO(OH)_2$. A spot test for cerium, employing benzidine in this manner, is quite specific within the group of rare earths; the sensitivity is 0.18γ Ce(1:275,000). The oxidation of benzidine to benzidine blue by higher oxides of metals can be used to detect these elements in mixtures.[267] The conversion of Pb^{++} ions to PbO_2 provides a selective test for lead.[268] As might be expected, from the participation of benzidine in autoxidation processes, the sensitivity of the tests for higher metal oxides such as PbO_2, is lower than the sensitivity of the tests for metals, which form higher oxides by autoxidation. For example, the benzidine spot test will reveal only 1γ Pb, in contrast to 0.15γ Mn, or 0.18γ Ce, which form autoxidizable hydrous oxides.

The foregoing tests are based on the reaction of insoluble higher metal oxides with benzidine involving, probably, participation of the latter in an autoxidation process. The site of the reaction is quite localized in such tests; consequently these are instances of topochemical reactions (see Chapter XI).

Redox reactions of benzidine in homogeneous systems are also known. They involve oxidants whose oxidation potentials are high enough to produce benzidine blue in acetic acid solution. For example, gold salts react with benzidine, in acetic acid solution, to produce free gold and benzidine blue.[269] This reaction can be applied to detect small amounts of gold.[270] The oxidation of benzidine by an acetic acid solution of chromate has been used for the detection of chromium;[271] the identifica-

[266] F. FEIGL, *Oesterr. Chem. Ztg.* **22**, 124 (1919).

[267] F. FEIGL, *Mikrochemie* **20**, 198 (1936); compare also Spot Tests, p. 161.

[268] F. FEIGL and A. SINGER, *Pharm. Presse* **6**, 37 (1938).

[269] G. MALATESTA and E. DI NOLA, *Chem. Abstracts* **8**, 1397 (1914).

[270] The benzidine test for gold was introduced into spot test analysis by N. A. TANANAEFF and K. A. DOLGOW, *Chem. Abstracts* **24**, 1313 (1930).

[271] N. A. TANANAEFF, *Z. anorg. allgem. Chem.* **140**, 327 (1924).

tion limit is 0.25γ Cr.   Monnier[272] found that neutral or weakly acetic acid solutions of persulfates oxidize benzidine to benzidine blue.   Since, under like conditions, no reaction is given by alkali peroxides, perborates, hydrogen peroxide, chlorates, perchlorates, bromates, and iodates, this test is highly selective for persulfate.   It can be carried out as a spot test.[273]

Any adequate discussion of the analytical application of the production of benzidine blue must emphasize the behavior of copper salts and molybdates.   As weak oxidants they are inactive toward benzidine, but their oxidizing power (oxidation potential) can be enhanced by the addition of certain materials.   Under such conditions, they oxidize benzidine to benzidine blue.   Effects are involved that can be included among the instances of enhanced reactivity discussed in Chapter V.   Feigl and Neuber[274] developed a selective test for copper based on this effect. Single drops of copper salt, benzidine acetate, and potassium bromide solutions are placed successively on filter paper.   A blue fleck appears with as little as 0.6γ Cu.   Alkali iodides, thiocyanates, and cyanides behave similarly to potassium bromide.   Obviously, alkali halides activate the action of copper on benzidine.   Moir[275] had previously found that a blue coloration appears when gaseous hydrogen cyanide is passed into a solution containing copper acetate and benzidine acetate.   Later, Sieverts and Hermsdorf[276] made this reaction the basis of a very sensitive test for cyanide.   Hence, the activator is detected in the test for cyanide by means of copper and benzidine, whereas the action of activated copper on benzidine is the basis of this test for copper.   .

The activation of cupric salts leading to the production of benzidine blue can be accounted for in two ways.   Both explanations take into account the redox reaction of cupric salts with the halide ions: $2Cu^{++} + 4Hal^- \rightarrow Cu_2Hal_2 + 2Hal^\circ$.   Accordingly, the products are: a slightly soluble cuprous halide (or a soluble complex cuprocyanide) and a free halogen (or halogen-like radical).   It seems reasonable to assume that the latter *in statu nascendi* oxidizes the benzidine to benzidine blue.   The other explanation is based on a consideration of the reversible redox reaction: Cu^{II} + benzidine $\rightleftharpoons$ benzidine blue + Cu^I.   The action of Cu^I on benzidine blue does not allow the equilibrium to lie far enough to the right to permit the formation of a visible ┬quantity of benzidine blue. Hence, cupric salts normally show no action with benzidine.   If, however,

[272] A. Monnier, *Chem. Abstracts* **11**, 426 (1917).

[273] Compare F. Feigl, Spot Tests, p. 242.

[274] F. Feigl and F. Neuber, *Z. anal. Chem.* **62**, 375 (1923).

[275] J. Moir, *Chem. News* **102**, 17 (1910).

[276] A. Sieverts and A. Hermsdorf, *Z. angew. Chem.* **34**, 3 (1921).

this reaction is carried out in the presence of halide ions (or halide-like ions), the univalent copper is effectively removed in a slightly soluble compound or sequestered in a soluble complex. Under such conditions, the univalent copper cannot exert its antagonistic action, and the divalent copper is then capable of oxidizing benzidine to benzidine blue.

An interesting activation toward benzidine can be obtained in the case of molybdates. Alkali molybdates, in acid solution, are inactive toward numerous reductants, or the action is feeble at most. However, the addition of a little phosphoric acid increases the oxidizing action of molybdates enormously. This enhanced oxidation is especially striking toward benzidine. Whereas, Mo^{VI} shows no action on benzidine, no matter what the pH of the solution, phosphomolybdic acid and its water-insoluble ammonium and potassium salts react immediately if the benzidine solution is buffered with ammonia or acetate. The reduction of the Mo^{VI} gives rise to a blue lower oxide (molybdenum blue), while benzidine blue is the oxidation product. This simultaneous production of two blue materials has been made the basis of an exceptionally sensitive spot test for phosphoric acid. Even invisible amounts of ammonium phosphomolybdate give a prompt reaction with benzidine.[277] It has been found that molybdate is activated not only by phosphoric acid, but also by arsenic and silicic acids, and likewise by germanic acid.[278] Tests have thus been made possible for silicic acid[279] and germanium. The activators for Mo^{VI} are invariably acids that are capable of producing heteropolyacids with molybdic acid. The author believes that the activation of Mo^{VI} is due to the formation of complexes in the molybdenum-bearing heteropolyacids.[280] Accordingly, these tests for P_2O_5,

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[277] F. FEIGL, *Z. anal. Chem.* **61**, 474 (1922); **74**, 386 (1928); **77**, 299 (1929); Spot Tests, p. 250.

[278] A. S. KOMAROWSKY and N. S. POLUEKTOFF, *Mikrochemie* **18**, 66 (1935).

[279] F. FEIGL and P. KRUMHOLZ, *Mikrochemie, Pregl Festschrift*, 1929, p. 82.

[280] It has been pointed out (see p. 118) that, according to P. KRUMHOLZ [*Z. anorg. allgem. Chem.* **212**, 97 (1933)] the catalysis by phosphoric acid of the Mo^{VI}—I^- reaction in acid solution is really due to the formation of $H_3PO_4 \cdot 12MoO_3$. This heteropolyacid is constantly regenerated as long as Mo^{VI} is present. Perhaps an analogous catalytic action is the basis of the activation of Mo^{VI} toward benzidine. However, another possible explanation can be offered. This is somewhat analogous to the idea that the activation of copper toward benzidine is due to the shifting of the equilibrium of the particular redox reaction. It may be assumed that the equilibrium lies far to the left in the reaction: Mo^{VI} + benzidine $\rightleftharpoons$ benzidine blue + Mo^V. If the Mo^V should become part of a complex phosphoheteropolyacid, the equilibrium is constantly disturbed in favor of the formation of benzidine blue. The studies of Krumholz strongly indicate the existence in acid solution of the heteropolyacid $H_3PO_4 \cdot 10MoO_3$. If this proposed mechanism proves valid, then the benzidine reaction of P_2O_5 (also As_2O_3 and GeO_2) is not due to the activation of Mo^{VI} in the heteropolyacid. Rather,

SiO_2, and GeO_2 can be considered fundamentally as tests for activators of the Mo^{VI}-benzidine reaction.

The color reactions of benzidine with oxidants and activated oxidants always involve the production of meriquinoid. oxidation products of benzidine. Consequently, homologues of benzidine can be expected to act similarly. Kulberg[281] has used o-tolidine (I) in place of benzidine for the detection of copper. He found that this substitution, combined with the use of ammonium thiocyanate, considerably increases the sensitivity (0.003γ Cu in 0.015 ml.). Schmidt and Hinderer[282] used 2,7-diamino-fluorene (II) for the detection of persulfate. This homologue gives a test that is about ten times as sensitive as when benzidine is used.

$$H_2N-\underset{\underset{CH_3}{|}}{\bigcirc}-\underset{\underset{CH_3}{|}}{\bigcirc}-NH_2 \qquad\qquad H_2N-\bigcirc\underset{\underset{H_2}{\overset{|}{C}}}{\bigcirc}-NH$$
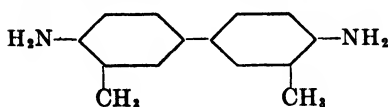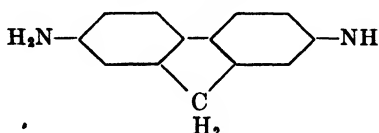
(I)   (II)

Consequently, it appears that o-tolidine and 2,7-diaminofluorene can be substituted for benzidine with advantage. However, comparative experiments have been made with these reagents only in the cases of copper and persulfate. Cullinane and Chard[282a] showed that 2,7-diaminodiphenylene oxide is an excellent reagent for detecting oxidizing compounds.

SPECIFIC AND SELECTIVE EFFECTS BASED ON CONDENSATION REACTIONS BETWEEN ORGANIC AND INORGANIC COMPOUNDS

It was shown in the preceding sections of this chapter that specific and selective precipitation and color reactions are connected with the presence of certain salt-forming groups in organic reagents. The term "salt-forming" is used here in its broadest sense, so that it covers both the production of normal binary salts by acidic or basic groups and the formation of complex compounds. The latter include: water-soluble and also insoluble intercalation and addition compounds, formed by the coordination of organic compounds with metal ions; insoluble inner complex salts; and electrolytes with inner complex anions. The discussion of selective actions exerted by organic derivatives of ammonia contained the first instance of a mode of reaction that has nothing to do with

the opposite would hold to a degree, namely, the deactivation (masking) of Mo^V because of its inclusion in an heteropolyacid. The activation of molybdenum toward benzidine undoubtedly is due to processes involving complex compounds, but the details of the mechanism have not yet been cleared up.

[281] L. KULBERG, *Mikrochemie* **20**, 153 (1936).
[282] J. SCHMIDT and W. HINDERER, *Ber.* **65**, 87 (1932).
[282a] H. M. CULLINANE and S. J. CHARD, *Analyst* **73**, 863 (1948).

salt formation. The particular case dealt with the participation of aromatic amines and diamines in redox reactions that resulted in the formation of colored oxidation products. The following discussion will deal with a type of reaction that likewise depends on the activity of groups, but which is definitely distinct from both salt-formations and redox reactions. It is known as condensation. This type of reaction, which is quite prevalent in preparative organic chemistry, can sometimes occur between inorganic and organic reactants. If it proceeds rapidly enough and leads to reaction products with characteristic properties, condensation can be utilized in analytical procedures.

Almost without exception, the condensations employed up to the present have involved a loss of water as a result of the action of certain groups on each other. Such reactions, so far as the inorganic participant is concerned, have been mostly confined to acidic or basic compounds. Usually, the water is eliminated without adding a dehydrating agent. Condensations of this kind sometimes lead to the formation of a precipitate. However, colored soluble compounds can result, or the products may be soluble compounds which, in their turn, give characteristic reactions. Condensations between organic and inorganic compounds are by no means as common as reactions that produce salts. Consequently, a far-reaching sensitivity is encountered almost always when condensation reactions are employed.

The Methylene Blue Reaction of Hydrogen Sulfide

For the first known instance of a reaction in which an organic reagent functioned by condensing with an inorganic material, rather than by forming a salt with the latter, we are indebted to Emil Fischer.[283] He found that hydrogen sulfide reacts with p-aminodimethylaniline (I) and ferric chloride to produce methylene blue (II):

(I)   (II)
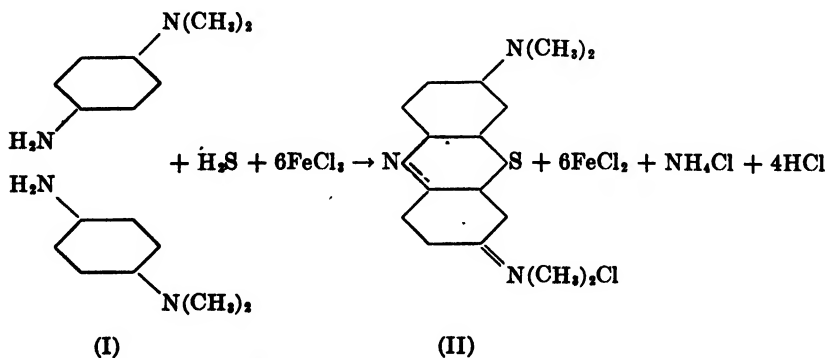
[283] E. FISCHER, *Ber.* **16**, 2234 (1883).

Although this stoichiometric equation gives a net representation of the formation of methylene blue, it is not a true picture of the course of the reaction. A reaction of the 9th order, such as is presented here, implies the simultaneous meeting of nine molecules. This possibility is most unlikely, and can occur, if at all, only at an immeasurable velocity. Therefore, the formation of methylene blue certainly proceeds in stages. The reaction, while not instantaneous, is rapid enough and goes far enough toward completion to be effective. It seems clear that an important role is played by the oxidation of (I), by the ferric chloride, to produce a *p*-quinoidal imide base[284] which actually appears as a component of the structure of methylene blue. A further likely assumption is that hydrogen sulfide does not take part directly in the reaction. Instead, the actual participant is probably free sulfur, since acidified ferric chloride solutions rapidly oxidize hydrogen sulfide to sulfur. Whatever the true reaction mechanism, such slight amounts of hydrogen sulfide are adequate to produce the dye that the methylene blue reaction has long been included among the most sensitive color reactions. Since the quantity of methylene blue produced is proportional to the amount of hydrogen sulfide, Mecklenburg and Rosenkränzer[285] were able to develop this reaction into a widely used colorimetric method for the determination of hydrogen sulfide and sulfides.

Condensation of Formaldehyde with Ammonia or Alkali Bisulfite

It is a general characteristic of aldehydes that the double bond between the carbon and oxygen atoms in the aldehyde group is easily opened in addition reactions. Formaldehyde displays this tendency to a particularly marked extent. Condensation reactions with ammonia or alkali bisulfite are of special interest in inorganic analysis, because the character of the inorganic component is completely altered in the resulting condensation products.

Formaldehyde differs from all other aldehydes with respect to its action toward ammonia. The others combine with ammonia, mole for mole, to form the respective aldehyde-ammonias. In contrast, six moles of formaldehyde unite with four moles of ammonia:

$$6CH_2O + 4NH_3 \rightarrow C_6H_{12}N_4 + 6H_2O$$
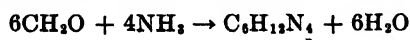
The product, known as hexamethylenetetramine, has the structural formula

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[284] Actually (I) is also a reagent for oxidizing materials with which it gives color reactions. See H. E. TREMAIN, *Ind. Eng. Chem., Anal. Ed.* **3**, 225 (1931).

[285] W. MECKLENBURG and F. ROSENKRÄNZER, *Z. anorg. allgem. Chem.* **86**, 146 (1914).
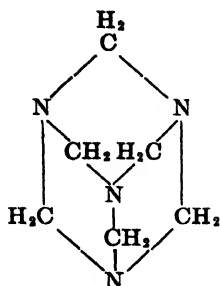
It is readily soluble in water, and has very slight basic properties.[286]   Its
dissociation constant is so low,[287] $K_b = 8 \times 10^{-10}$, that, in contrast to
ammonia, it does not redden phenolphthalein solution.   This diverse
behavior was used by Kolthoff[288] as the basis of an elegant titrimetric
method for determining ammonium salts.   In this procedure, a solution
of the ammonium salt is treated with an excess of neutral formaldehyde
and a few drops of phenolphthalein as indicator.   Alkali hydroxide is then
added drop by drop.   The liberated ammonia is immediately recaptured
by the formaldehyde with production of hexamethylenetetramine.   A
permanent red is obtained only after all the ammonium salt has been
decomposed and a slight excess of the standard base is present.[289]   The
ability to condense with formaldehyde is retained in the organic deriva-
tives of ammonia.   The so-called Schiff's bases are formed with primary
amines:

$$R-NH_2 + CH_2O \rightarrow R-N=CH_2 + H_2O$$
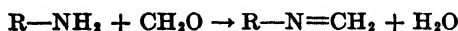
(The name base is scarcely justified, since the basic character of these
products is very weak.)   The condensation ability of the NH_2 group in
amino carboxylic acids is quite important.   The latter are internal salts
in which the amino group and the neighboring carboxyl group saturate
themselves intramolecularly.   In aqueous solution they dissociate to
form oybrid ions.   On treatment with alkali hydroxide, the NH_2 is
set free:

$$^+NH_3-R-COO^- + OH^- \rightarrow H_2N-R-COO^- + H_2O$$
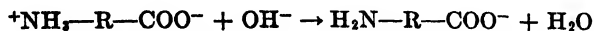
If the alkalization is carried out in the presence of formaldehyde, the

[286] Nevertheless the basicity is sufficient to accomplish a quantitative precipita-
tion of metal oxyhydrates or basic salts from hydrolyzable metal salt solutions.   For
pertinent literature see F. J. WELCHER, *op. cit.*, Vol. III, p. 124*ff*.

[287] I. M. KOLTHOFF, Volumetric Analysis, Vol. II, p. 163.   New York, 1929.

[288] I. M. KOLTHOFF, *Pharm. Weekblad* **58**, 1463 (1921); see also K. MARCALI and
W. RIEMAN, *Ind. Eng. Chem., Anal. Ed.* **18**, 709 (1946).

[289] It is perfectly legitimate to assume that ammonium salts react directly: $4NH_4^+$
$+ 6CH_2O \rightleftharpoons (CH_2)_6N_4 + 4H^+ + 6H_2O$, provided it is further accepted that the
ammonia produced by the hydrolysis of ammonium salts enters into the formation of
hexamethylenetetramine by the condensation reaction given in the text.

latter reacts with the NH_2 group:

$$H_2N-R-COO^- + CH_2O \rightarrow H_2C=N-R-COO^- + H_2O$$
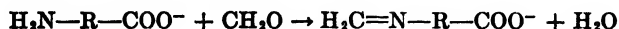
This effect is the basis of the well-known formol titration, which Sörensen[290] developed for the alkalimetric determination of amino acids. This method has acquired great importance in organic analysis, and particularly in biochemistry.[291]

The behavior of formaldehyde toward alkali bisulfite is entirely analogous to that of other aliphatic and aromatic aldehydes. However, the aqueous-solubility of formaldehyde allows the reaction to take place instantly and quantitatively. In all cases, the carbon-oxygen double bond of the carbonyl group is opened, and the bisulfite radical is added:

$$R-C\underset{H}{\overset{O}{<}} + NaHSO_3 \rightarrow R-C\underset{SO_3Na}{\overset{H \quad OH}{<}}$$
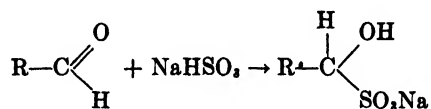
The normal sulfites are readily oxidized to sulfate by iodine, but this characteristic is completely lost in the aldehyde-bisulfite compounds.[292] Kurtenacker[293] used the rapid formation of formaldehyde-bisulfite and its resistance to iodine in his iodometric method of determining alkali thiosulfate when mixed with sulfite. It is merely necessary to add an excess of formaldehyde to the solution of the alkali salts, and then acidify with acetic acid (to prevent the oxidation of formaldehyde by iodine). The unchanged thiosulfate is then titrated in the usual way with standard iodine solution.[294] The difference in the behavior of sodium thiosulfate and sodium selenosulfate toward formaldehyde is quite remarkable. As already stated, thiosulfate remains unchanged. Sodium selenosulfate, in contrast, acts as though it is a very loose combination of sodium sulfite and selenium. Accordingly, its reaction with formaldehyde produces aldehyde bisulfite, and deposition of red elementary selenium. In this way, $Na_2S_2O_3$ and Na_2SSeO_3 can be rapidly differentiated, and small

[290] S. P. L. SÖRENSEN, Biochem. Z. 7, 43 (1907); 25, 1 (1910); Z. physiol. Chem. 63, 27 (7909); 64, 120 (1910).

[291] R. WILLSTÄTTER and E. WALDSCHMIDT-LEITZ, Ber. 54, 2968 (1921).

[292] Concerning the constitution of the aldehyde bisulfite compounds see F. RASCHIG and W. PRAHL, Ann. 448, 265 (1926); G. SCHROETER, Ber. 59, 2341 (1926); 61, 1616 (1928).

[293] A. KURTENACKER, Z. anal. Chem. 64, 56 (1924).

[294] Toward formaldehyde, bisulfites react analogously to sulfites. The reaction produces aldehyde-bisulfite and one equivalent of alkali hydroxide:

$$Na_2SO_3 + CH_2O + H_2O \rightarrow CH_2(OH)(SO_3Na) + NaOH$$
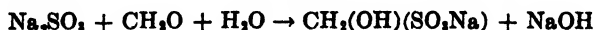
amounts of the latter can be detected in the presence of large amounts of thiosulfate.[295]

Zil'berman and Markowa[296] described an interesting application of the condensation of formaldehyde with sulfite. (Hyposulfite behaves like sulfite.) They used the fact that barium chloride produces no precipitate when added to cold solutions of aldehyde-bisulfite. Consequently, after adding an excess of formaldehyde, a satisfactory sulfate determination by precipitation as $BaSO_4$ can be made in the presence of SO_3^{--} and $S_2O_4^{--}$ ions.

Condensation of Aromatic Aldehydes with Hydrazine

Benzaldehyde and other aromatic aldehydes, as distinguished from aliphatic aldehydes, condense with hydrazine and its salts. Water is lost, and "aldazines" result. The latter are water-insoluble compounds that exhibit no acidic or basic functions. The condensation occurs at room temperature in aqueous solution. It can be represented by the general equation:

$$2R-CHO + H_2N-NH_2 \rightarrow R-\overset{H}{\underset{|}{C}}=N-N=\overset{H}{\underset{|}{C}}-R + 2H_2O$$
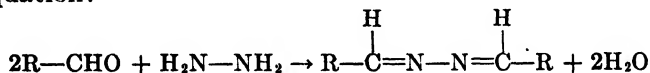
Fichter and Goldach[297] employed the formation of benzaldazine from benzaldehyde and hydrazine for the quantitative gravimetric determination of hydrazine. The aldazine, which carries down a little benzaldehyde, was washed with water, dried at 85°C., and then weighed. Feigl and Schwarz[298] recommended that the benzaldehyde be replaced in this determination by o-hydroxybenzaldehyde (salicylaldehyde), which is far more soluble in water. Its solubility in water is sufficient to produce a readily discernible precipitate or turbidity with hydrazine, which can thus be detected. In contrast, benzaldehyde, cannot be used in this way because the separation of benzaldehyde from its alcohol solutions causes turbidities when added to water solutions. As little as 0.1γ hydrazine can be detected if an acetic acid solution of salicylaldehyde is used. Since this aldehyde produces a water-soluble oxime when it reacts with hydroxylamine, 1γ hydrazine can be detected in the presence of 4000γ hydroxylamine, provided a sufficient excess of the aldehyde is used.

It is rather striking that, although salicylaldehyde, because of its OH group, is more soluble than benzaldehyde (see p. 396), it nevertheless produces an aldazine that is less soluble than benzaldazine. Conse-

[295] F. Feigl and P. West, unpublished studies. Compare A. Brukl and W. Maxymowicz, Z. anal. Chem. 68, 16 (1928).

[296] Y. J. Zil'berman and N. G. Markowa, Chem. Abstracts 40, 1426 (1946).

[297] Fr. Fichter and A. Goldach, Helv. Chim. Acta 15, 1513 (1932).

[298] F. Feigl and R. Schwarz, Rec. trav. chim. 58, 474 (1939).

quently, salicylaldazine probably has the ring structure of an inner complex salt:
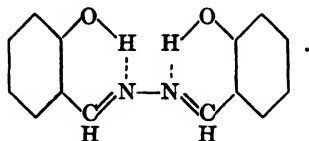
A fact in keeping with this suggestion is the bright yellow color of salicyl-aldazine, whereas benzaldazine is colorless. Obviously, in this inner complex group, the phenolic OH group has lost its solubility-promoting action entirely, or for the most part. However, it shows a bathochromic effect.

Feigl found that hydrazine can be quantitatively determined by means of the condensation with salicylaldehyde. The resulting aldazine can be successfully filtered, washed, dried, and weighed. It would be interesting to learn the behavior of colored aromatic aldehydes (*e.g.*, dimethylamino-benzaldehyde) on condensation with hydrazine. Such studies might result in the discovery of reagents for hydrazine that would produce colored aldazines, or aldazines whose colors differ from those of the parent aldehydes. The sensitivity of the aldazine test would surely be increased by such modifications.

Condensation Reactions of Diacetylmonoxime and Salicylaldehyde with Hydroxylamine

The reducing powers of hydroxylamine can be used for its identifica-tion and quantitative determination only in the absence of other reduc-tants. Consequently, the fact that the NOH group of hydroxylamine can be readily introduced into organic compounds containing the CO group is of analytical significance. This oximation process removes the reducing power of hydroxylamine, but confers on it acid characteristics and also the ability to form inner complex salts. The coordination formula of the red inner complex nickel salt of diacetylmonoxime shows that the hydrogen of one of the two NOH groups is replaced by an equivalent of nickel, while the nitrogen atom of the second NOH group is coordinated to the nickel by an auxiliary valence bond (see p. 271). In the inner complex copper salt of salicylaldoxime, the metal takes the place of the phenolic hydrogen and is coordinatively linked to the NOH group by auxiliary valences (see p. 197). It is entirely in line with the great tendency toward formation of inner complex salts that these two salts can be prepared by methods other than the usual reaction of copper and nickel solutions with the respective organic reagents. These salts are also produced if the oxime reagents are formed, with the aid of hydroxyl-

amine, in the presence of Ni^{++} or Cu^{++} ions. Such syntheses of the inner complex salts from the three necessary components can be used for the detection, and, presumably, also for the quantitative determination of hydroxylamine.

Hirschl and Verhoeff[299] used the ease of oximating diacetylmonoxime by hydroxylamine in ammoniacal solution in the presence of Ni^{++} or $[Ni(NH_3)_2]^{++}$ ions to produce a direct precipitation of red Ni-diacetyl-dioxime. The following reaction occurs:

$$CH_3-C=O \atop CH_3-C=NOH + NH_2OH + \frac{1}{2}Ni^{++} + OH^- \rightarrow CH_3-C=N \atop CH_3-C=N-OH Ni/2 + 2H_2O$$
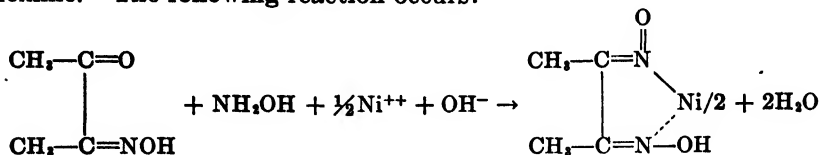
Consequently, an ammoniacal solution containing nickel and diacetyl-monoxime can be used as a reagent for hydroxylamine. The formation of the red nickel salt permits the detection of as little as 10γ NH_2OH in 2 ml. The reaction can also be conducted as a spot test on filter paper impregnated with the reagent solution. In this form, the test has an identification limit of 1γ NH_2OH.

The direct production of the light yellow inner complex Cu-salicyl-aldoxime from the necessary ingredients (salicylaldehyde, hydroxylamine, copper acetate) has been recommended by Feigl and Schwarz[300] for the detection of hydroxylamine. The reagent consists of a freshly prepared mixture of (a) salicylaldehyde in dilute acetic acid and (b) copper acetate-acetic acid solution. Oximation and salt-formation occur on the addition of hydroxylamine:

$$\text{(salicylaldehyde)} + NH_2OH + \frac{1}{2}Cu(C_2H_3O_2)_2$$

$$\rightarrow \text{(Cu-salicylaldoxime complex)} + CH_3COOH + H_2O$$
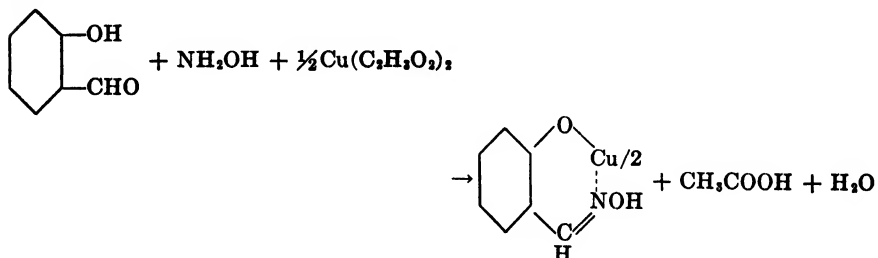
This test also can be carried out as a spot reaction; the identification limit is then 1γ NH_2OH.

The foregoing procedures, in which the formation of inner complex salts from three ingredients is utilized, can also be applied for the detection of an organic component. Neuberg and Scheuer[301] showed that

[299] W. H. HIRSCHL and J. A. VERHOEFF, *Chem. Weekbl.* **20,** 319 (1923).

[300] F. FEIGL and R. SCHWARZ, *Rec. trav. chim.* **58,** 475 (1939).

[301] C. NEUBERG and M. SCHEUER, *Monatsh.* **54,** 1031 (1929).

traces of diacetyl can be revealed by the combined action of hydroxyl-amine and a nickel salt.   Nickel dimethylglyoximate is formed:

$$
\begin{array}{l}
\text{CH}_3\text{—C}\text{=}\text{O} \\
\qquad\qquad\qquad + 2\text{NH}_2\text{OH} + \tfrac{1}{2}\text{Ni}^{++} \rightarrow \\
\text{CH}_3\text{—C}\text{=}\text{O}
\end{array}
\qquad
\begin{array}{l}
\text{CH}_3\text{—C}\text{=}\text{N}\text{=}\text{O} \\
\qquad\qquad\qquad\text{Ni}/2 + 2\text{H}_2\text{O} + \text{H}^+ \\
\text{CH}_3\text{—C}\text{=}\text{N—OH}
\end{array}
$$
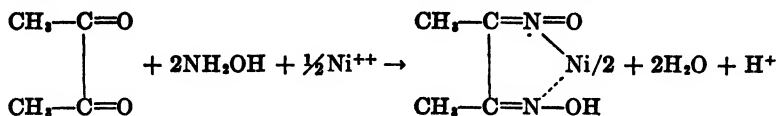
No other instance of the formation of a salt is known which can be considered from so many standpoints, and utilized in such a variety of ways, as the production of nickel diacetyldioxime (dimethylglyoxime). This is the justification for the following compilation, even though the topic does not lie entirely within the scope of this text.   Nickel dimethyl-glyoximate is the classic example of inner complex compounds.   It can be prepared in the solid form by the following methods, and applied in ways that are valuable both from the analytical and didactic points of view:

(1) Diacetyl + $[\text{Ni}(\text{NH}_3)_4]^{++}$ + NH_2OH — For detection of diacetyl

(2) Diacetylmonoxime + $[\text{Ni}(\text{NH}_2)_4]^{++}$ — For detection of hydroxylamine or diacetylmonoxime

(3) Diacetyldioxime $(=\text{DH}_2)$ + $[\text{Ni}(\text{NH}_3)_4]^{++}$ — For detection and quantitative determination of nickel or diacetyldioxime

(4) Solutions in which the equilibrium Ni^{++} + $2\text{DH}_2 \rightleftharpoons \text{Ni}(\text{DH})_2$ + 2H^+ is disturbed by basic materials — For detection of basic materials (see p. 661) and to illustrate chemical equilibria

(5) Solid $\text{Ni}(\text{CN})_2$ and solid DH_2 at 180°C. — To illustrate the reactivity of solids in the absence of a solvent[301]

(6) Solid Ni-8-hydroxyquinoline and solid DH_2 at 150°C. — To illustrate the reactivity of solids and transformation of inner complex salts[302]

(7) Yellow solutions of $\text{Ni}(\text{DH})_2$ in molten naphthalene or oleic acid, on cooling — To illustrate the solubility of inner complex salts in organic liquids, and abnormal solution colors

(8) $\text{Ni}(\text{DH})_2$ vapor by condensation (vacuum sublimation) — To illustrate the exceptional tenacity of the metal binding in inner complex salts

(9) $\text{Ni}(\text{DH})_2$-paper reacting with Pd^{++} — To illustrate the protective layer effect (p. 663) and to detect traces of palladium[303]

Selective Condensation Reactions of Salicylaldehyde by Formation of Inner Complex Salts

More than a century ago Ettling[303a] observed that salicylaldehyde (I) yields insoluble compounds when treated with ammoniacal solutions of

[301] F. Feigl, L. I. Miranda and H. A. Suter, *J. Chem. Education* **21**, 20 (1944).

[302] F. Feigl, *Chemistry & Industry* **57**, 1161 (1938).

[303a] C. Ettling, *Ann.* **35**, 265 (1840).

nickel or copper salts. Later, Schiff[303b] stated that these products were salts of salicylimine (II), formed by a condensation reaction of ammonia and salicylaldehyde. He also found that primary amines could replace ammonia in the reaction and thus give rise to the production of N-alkyl-salicylimines. Such condensation products of nitrogen bases and aldehydes are now commonly known as Schiff's bases. The reaction of ammoniacal solutions of salicylaldehyde with copper and nickel salts to produce insoluble salts of the imine is not self-explanatory, since no imine of the formula (II) is isolable from water-ammoniacal solutions of salicylaldehyde. In all likelihood, no imine of this kind exists at all in the free state. Ammonium salts of the phenolic aldehyde are present in the ammoniacal solution of salicylaldehyde. This is shown by the fact that this solution has the same yellow color as solutions of salicylaldehyde in alkali hydroxides.[303c] Hence, it is a justifiable question as to why a reagent solution that contains no imine produces precipitates of the metal salicylimines when copper or nickel salts are brought together with ammoniacal solutions of salicylaldehyde. Pfeiffer and his associates cleared up this seeming contradiction in a paper that is one of the classics in the literature of complex chemistry.[303d] They found that Mg^{++} and Ca^{++} ions react with ammoniacal solutions of salicylaldehyde to form nitrogen-free salts of the structure (III). This finding is in accord with the presence and action of unchanged salicylaldehyde. On the other hand, Cu^{++}, Ni^{++}, and Zn^{++} ions do not form normal salts of salicyl-aldehyde. Instead, they produce insoluble, inner complex salts of salicylimine having the coordination formula (IV). If normal Cu, Ni, and Zn salts of salicylaldehyde of formula (III) are prepared, and subsequently treated with ammonia, they are promptly converted to inner complex salts of formula (IV). Other o-hydroxyaldehydes behave analogously to salicylaldehyde. Likewise, o-hydroxyketones, such as o-hydroxyacetophenone (V), which forms no imine in water-ammonia solution, produces inner complex salts of type (VII) with ammoniacal metal salt solutions.

[303b] H. SCHIFF, *Ann.* **150**, 197 (1869).

[303c] Experience shows that color changes are never brought about when normal alkali salts of acidic organic compounds are formed without alteration of the constitution of the organic component. Hence, it is probable that the yellow color produced by dissolving the colorless salicylaldehyde in ammonia or alkali hydroxide is due to the fact that, in the salts, there is a coordination of the nitrogen or alkali atom to the oxygen atom of the aldehyde group (inner complex binding). This blocking of the CO group in the ammonium salt of salicylaldehyde provides a plausible explanation of why no, or only a slight, condensation can occur with ammonia to form imine.

[303d] P. PFEIFFER, E. BUCHHOLZ and O. BAUER, *J. prakt. Chem.* **129**, 163 (1931).
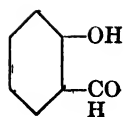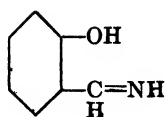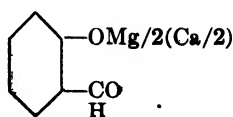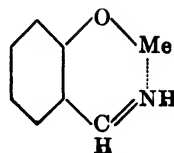
| (I) | (II) unstable | (III) | (IV) stable
Me = ½Cu,
½Zn, etc. |

| (V) | (VI) unstable | (VII) stable |
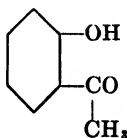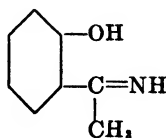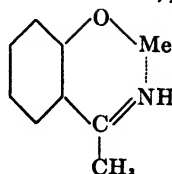
The behavior of ammoniacal solutions of *o*-hydroxyaldehydes and *o*-hydroxyketones shows, therefore, that imines, which are innately unstable, are stabilized by formation of inner complex salts or, more correctly, by incorporation in inner complex salts. Accordingly, the reaction of ammoniacal solutions of salicylaldehyde with Cu^{++} ions, *etc.*, should not be formulated as the reaction of an imine, but rather as a condensation reaction brought about by the production of an inner complex:
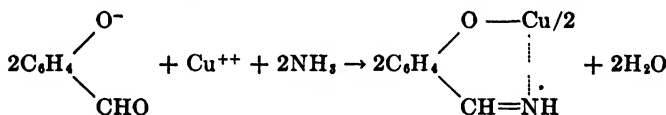
The coordination formulas (IV) and (VII) of inner complex salts of the imines of salicylaldehyde and *o*-hydroxyacetophenone not only have identical inner complex rings, but they also exhibit a similarity to the ring closures of the inner complex salts of salicylaldoxime (see p. 196). Consequently, the precipitating action of salicylaldehyde could be regarded from the standpoint of the activity of a particular arrangement of groups, namely, a phenolic OH group adjacent to a noncyclically bound, tertiary, coordinatable N atom. It seems preferable, however, to consider the activity of salicylaldehyde in ammoniacal solution from the standpoint of a condensation reaction brought about by the formation of an inner complex, because the precipitating reagent in this case is not isolable as such.

Attention should be directed to the fact that numerous examples are given in this chapter of a stabilization of organic compounds, or of certain of their tautomeric forms, by complex binding. These instances include the following: (a) the stabilization of rhodizonic acid in its inner complex

barium and lead salts, that are not soluble in dilute acids (see p. 174); (b) the stabilization of dienol-thallium salts through coordination of carbon bisulfide (see p. 208); (c) the stabilization of the innately readily oxidizable thionalid in its inner complex salts as well as the incorporation of the naturally unstable enol forms of thioglycolic acid anilide and of thionanilid in stable cobalt complex salts (see p. 230); (d) the ability of dimethylglyoxime, when bound to palladium in an inner complex, to form salts of a palladium-dimethylglyoxime acid (see p. 276); (e) the stabilization of an enol form of 6-nitroquinoline through formation of a palladium salt (see p. 284).   Additional instances will be furnished by the acidification of polyhydroxy compounds by boric acid because of the formation of esters and condensation (see p. 356), and by the production of metal-pyrocatechol acids through the formation of inner complex anions of pyrocatechol (see p. 361).   To some extent, the stabilization of organic components in complex compounds is a counterpart to the stabilization of anomalous or less stable valence stages of metals in complex salts, a finding that has been emphasized several times in this text.   Obviously, the possibility of stabilizing organic compounds, or certain of their isomeric forms, through complex binding is of fundamental importance. In this way, the range of action of organic compounds can be broadened and this extension can be significant in securing specific or selective effects.

Duke[302a] studied the analytical use of ammoniacal solutions of salicylaldehyde.   He found that only Cu^{++}, Ni^{++}, V^{++}, Pd^{++}, and Fe^{++} ions produce a precipitate from dilute salt solutions, which have been masked with alkali tartrate against hydroxide precipitation.   Although not all ionic species have been studied as yet, and the behavior of concentrated solutions is still to be tested, the available findings show that a remarkable selectivity exists.   Furthermore, the precipitation sensitivity is quite satisfactory.   The mechanism proposed by Pfeiffer and his associates for the stabilization of imines through complex binding doubtless also applies to the precipitations by salicylaldehyde from ammoniacal solutions.   Duke investigated also the behavior of ammoniacal solutions of 5-nitro-, 5-bromo-, and 3,5-dibromosalicylaldehyde, and likewise the action of monomethylamine solutions of salicylaldehyde and its derivatives.   (The writer believes that with monoalkyl amines there may be a possibility of forming stable Schiff's bases without the production of an inner complex.)   As might have been expected, the precipitating action of the derivatives is analogous to that of salicylaldehyde; all of the precipitates are formed only in alkaline solution, and the precipitated products are decomposed by dilute acids.   Table **X** shows the results

[302a] F. R. Duke, *Ind. Eng. Chem., Anal. Ed.* **16**, 750 (1944).

obtained with salt solutions, which contained 0.1–0.2% metal and 5% sodium tartrate. The figures in parentheses are the identification limits (in γ/ml.) of the precipitation reactions.

TABLE X

Reactions of Salicylaldehyde and Derivatives

Ion	Salicylaldehyde		5-Nitro		5-Bromo		3,5-Dibromo	
	NH₃	CH₃NH₂	NH₃	CH₃NH₂	NH₃	CH₃NH₂	NH₃	CH₃NH₂
Cu^{++}	Green (2) ppt.	Green (0.75) ppt.	Green (3.5) ppt.	Green (1.5) ppt.	Green (4) ppt.	Green (1.5) ppt.	Green (4) ppt.	Green (2) ppt.
Ni^{++}	Orange (2) ppt.	Yellow (0.75) ppt.	Orange (3) ppt.	Yellow (1) ppt.	Yellow (3) ppt.	Yellow (2) ppt.	Brown (3) ppt.	Yellow (1.5) ppt.
V^{++}	Red ppt.	Red ppt.	Orange ppt.	Red ppt.	Red ppt.	Red ppt.	Red ppt.	Red ppt.
Pd^{++}	Yellow ppt.	Yellow ppt.	Yellow ppt.	Yellow ppt.	Yellow ppt.	Yellow ppt.	Yellow ppt.	Yellow ppt.
Mn^{++}	....	....	....	....	....	....	....	Brown ppt
Fe^{+++}	Red ppt.	Red ppt.	....	....	Red ppt.			
Fe^{++}	Red color	Red ppt.	Red color	Blue ppt.	....	Lavender ppt.	. . . . .	Purple ppt.
Co^{++}	....	Brown (0.5) ppt.	Brown (4) ppt.	Brown (0.75) ppt.	Brown (1.05) ppt.	Brown (1) ppt.	Brown (2) ppt.	Brown (1.5) ppt.
Hg^{++}	....	....	....	....	....	....	....	Yellow ppt.
Zn^{++}	....	....	....	....	....	....	....	Yellow ppt.
Cd^{++}	....	....	....	....	....	....	....	Yellow ppt.
ReO_4^{-}	....	....	....	....	....	....	....	Yellow ppt.

The foregoing figures show that it makes a difference whether ammonia or methylamine is used as solvent for salicylaldehyde and its derivatives. A definite influence is exerted by the entrance of =NCH₃ instead of =NH into the inner complex ring. In general, the CH₃ group enhances the insolubility; in certain cases it even influences the color of the precipitates. The influence is exhibited especially in the case of 3,5-dibromosalicylaldehyde. Inner complex salts of the methylimine of this aldehyde are so slightly soluble that seemingly it exhibits no precipitation selectivity. This finding is very instructive because it shows that, under some circumstances, the selective action of a salt-forming group in an organic compound can completely disappear because of the presence or introduction of groups or atoms that exert a size effect (compare Chapters VIII and IX).

According to Duke, the precipitation of the inner complex copper and nickel salts of salicylimine permits excellent gravimetric methods of determining these metals, since the precipitates remain unchanged on drying. The writer thinks it a remarkable fact that palladium is precipitated from ammoniacal solution by salicylaldehyde and its derivatives. It was pointed out in this chapter that precipitation of

inner complex palladium dimethylglyoximate and palladium-1-nitroso-2-naphtholate does not occur from ammoniacal solution, because of the presence of the very stable complex $[Pd(NH_3)_2]^{++}$ ions. The precipitation of palladium from ammoniacal solution by o-hydroxyaldehydes signifies, therefore, that the resulting inner complex salts have a lower solubility product than the inner complex salts of palladium with dimethylglyoxime and 1-nitroso-2-naphthol. Accordingly, there appears to be a possibility for use of this reagent for gravimetric determination of palladium. It would also be interesting to learn whether condensation of o-hydroxyaldehydes and o-hydroxyketones with primary aliphatic amines would yield stable, ammonia-soluble products of the type of Schiff's bases, which might then serve as selective precipitants.

Condensation Reactions of 2,4-Diamino-6-Hydroxypyrimidine and Chrysean with Nitrous Acid

Traube[304] found that 2,4-diamino-6-hydroxypyrimidine (I) reacts with nitrous acid to form 2,4-diamino-5-nitroso-6-hydroxypyrimidine (II) or (IIa):

$$
\begin{array}{ccc}
\begin{array}{c}
N\!=\!C\!-\!OH \\
| \quad | \\
H_2N\!-\!C \quad CH \\
\| \quad \| \\
N\!-\!C\!-\!NH_2 \\
\text{(I)}
\end{array}
+ HONO \rightarrow
\begin{array}{c}
N\!=\!C\!-\!OH \\
| \quad | \\
H_2N\!-\!C \quad C\!-\!NO \\
\| \quad \| \\
N\!-\!C\!-\!NH_2 \\
\text{(II)}
\end{array}
\quad or \quad
\begin{array}{c}
N\!=\!C\!-\!OH \\
| \quad | \\
H_2N\!-\!C \quad C\!=\!NOH \\
\| \quad \| \\
N\!-\!C\!=\!NH \\
\text{(IIa)}
\end{array}
\end{array}
$$
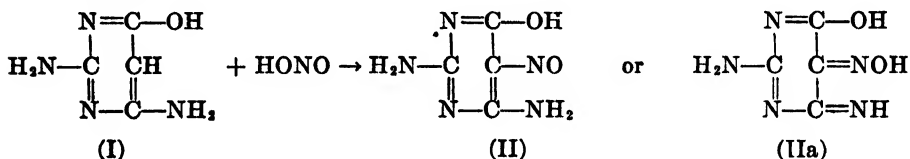
The strawberry colored product has neither acidic nor basic properties, which probably accounts for its insolubility in water. In contrast, (I) is a strong base which combines with mineral acids to produce water-soluble salts. Perhaps the nitroso compound has the isonitroso structure (IIa), which would explain how the basic character of the residual NH_2 group is nullified, namely by the acidic NOH group. Hahn[305] used the precipitation of the colored nitroso compound as a test for nitrite; 12γ NO_2^- can be detected in 1 ml. This reagent has the advantage that nitrates do not react with it. Accordingly, it can be used in the preparation of nitrite-free nitrate solutions.[306] It is not satisfactory for gravimetric determinations; the values obtained are +0.4 to −2% away from the actual nitrite content.

[304] W. TRAUBE, *Ber.* **33**, 1871 (1900).
[305] F. L. HAHN, *Ber.* **50**, 705 (1917).
[306] This method of removing nitrite by precipitation is more important from the theoretical than the practical standpoint. Nitrite can be completely removed from nitrate solutions, without resorting to precipitation, by reaction: with urea [compare A. CLAUS, *Ber.* **4**, 142 (1871)]; with hydrazoic acid [F. SOMMER and H. PINCAS, *Ber.* **48**, 1968 (1915)]; with amidosulfonic (sulfamic) acid [P. BAUMGARTEN and I. MARGGRAFF, *Ber.* **63**, 1019 (1930)].

A condensation, analogous to the one just discussed, probably occurs when nitrous acid acts on chrysean. A dark brown precipitate is formed. Chrysean is a thiazole derivative; it can be represented by (I) or (II):

$$H_2C-N \quad S$$
$$HN=C \qquad C-C-NH_2$$
$$S$$

$$HC-N \quad S$$
$$H_2N-C \qquad C-C-NH_2$$
$$S$$

(I)   (II)
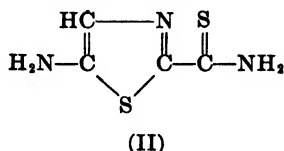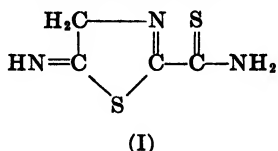
These formulas indicate that the NO group of the nitrous acid may replace an H atom in either a CH_2 group or a CH group of the chrysean. Dubsky and his collaborators[307] report that nitrite can be detected by treating the test solution with an alcoholic acidified solution of chrysean. A red coloration develops at first, and then a dark brown precipitate forms. As a spot reaction, this test has a sensitivity of 0.25 γ nitrite in drops.

Condensation of 1,8-Diaminonaphthalene with Nitrous Acid or Selenious Acid

The *peri*-situated NH_2 groups of 1,8-diaminonaphthalene (1,8-naph-thalenediamine) (I) or their H atoms, are capable of participating in condensation reactions that result in 6-membered ring closures. The stability of such rings is doubtless responsible for the occurrence of condensation reactions involving 1,8-diaminonaphthalene, whereas the analogous aromatic diamines, with the NH_2 groups in the *ortho* position, either do not react or the reaction takes a different course.[308] Condensation in these latter cases can result only in 5-membered rings. The reactions of 1,8-diaminonaphthalene with nitrous or selenious acid have analytical significance because of their high selectivity. These condensations have been known for a long time, but their application in spot test analysis is fairly recent.[309]

An orange-red precipitate of 1,8-azimidonaphthalene (II) is formed by the action of nitrous acid on sulfuric acid solutions of 1,8-diamino-naphthalene.[310] The reaction occurs almost instantaneously on gentle warming and no dehydrating agent is necessary:

$$\begin{array}{c} -NH_2 \\ -NH_2 \end{array} + \begin{array}{c} O \\ HO \end{array}N \rightarrow \begin{array}{c} -N \\ -N \\ H \end{array}N + 2H_2O$$

(I)   (II)
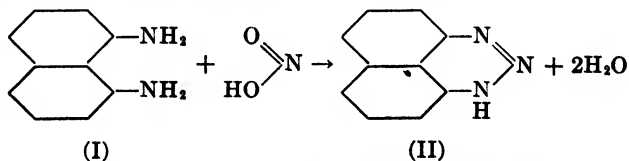
[307] J. V. Dubsky, J. Triflek and A. Okÿc, *Mikrochemie* **15**, 99 (1934).

[308] Compare F. Sachs, *Ann.* **365**, 150 (1909); O. Hinsberg, *Ber.* **22**, 866 (1899); G. T. Morgan and W. Godden, *J. Chem. Soc.* **97**, 1719 (1910).

[309] F. Feigl, Spot Tests, pp. 249, 266.

[310] A. de Aguiar, *Ber.* **7**, 315 (1874).

The identification limit, when carried out as a spot test, is 0.1γ HNO_2. If selenious acid is absent (see *infra*) the test is specific for nitrite, since other colorless acids, *e.g.*, sulfuric, produce only colorless insoluble salts, if they react at all. Although the requisite studies have not been made, it is entirely possible that the production of a precipitate by nitrite may be adaptable to quantitative purposes, especially since the normal salts of 1,8-diaminonaphthalene with mineral acids are soluble in hot water.

Hinsberg[311] found that 1,8-diaminonaphthalene gives an interesting reaction with selenious acid. The initial reaction produces a yellow-red precipitate of dihydrodi-*peri*-naphthoselenodiazole (III):

(III)
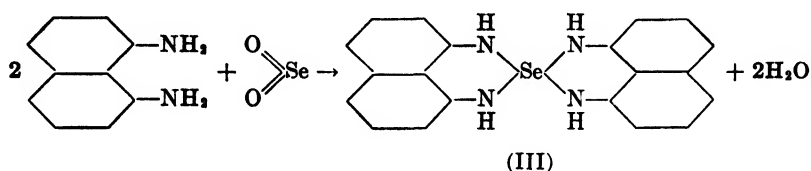
This product undergoes autoxidation and rapidly produces brown di-*peri*-naphthoselenodiazole (IV):

(III)

(IV)
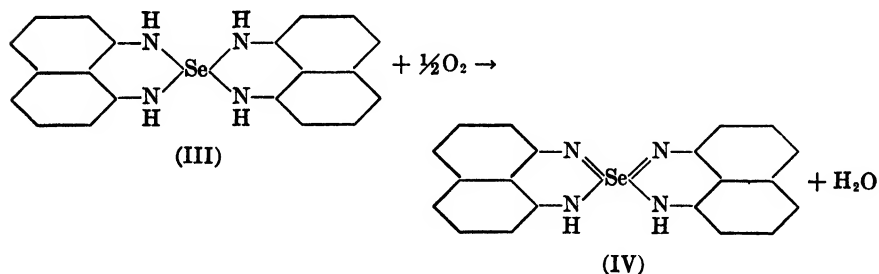
Accordingly, in this instance a condensation reaction is combined with an oxidation ($Se^{IV} \rightarrow Se^{VI}$).

When only small quantities of selenium are present, (IV) forms directly, while with considerable amounts of SeO_2, it is possible to obtain oxidation of (III) to (IV) by means of H_2SeO_3 itself. In this latter case free selenium precipitates. As little as 1γ SeO_2 can be detected. Selenic acid likewise produces (IV). The question is still open as to whether direct condensation occurs or whether a preceding reduction to selenious acid takes place. Under suitable conditions a satisfactory gravimetric method for selenium can probably be developed, with (IV) as the final form to be weighed. The present gravimetric procedures involve the weighing of free selenium produced by reduction of the sample. Consequently, the suggested method would offer considerable advantage,

[311] O. HINSBERG, *Ber.* **52**, 21 (1919).

especially in view of the fact that tellurous acid does not react with 1,8-diaminonaphthalene.[311a]

Oxidative Condensation of 8-Hydroxyquinoline with Hydroxylamine

The ability of hydroxylamine, in alkaline solution, to add itself to active carbon double bonds and, after inner-molecular reduction, to form an amine, is also shown with 8-hydroxyquinoline. The initial reaction produces 5-amino-8-hydroxyquinoline (I), which reacts with excess 8-hydroxyquinoline, with concurrent oxidation by the oxygen of the air.[312] The result is 5,8-quinolinequinone-(8-hydroxy-5-quinolylimid) the structure of which is shown by (II):

(1)

(I)

(2)

(II)
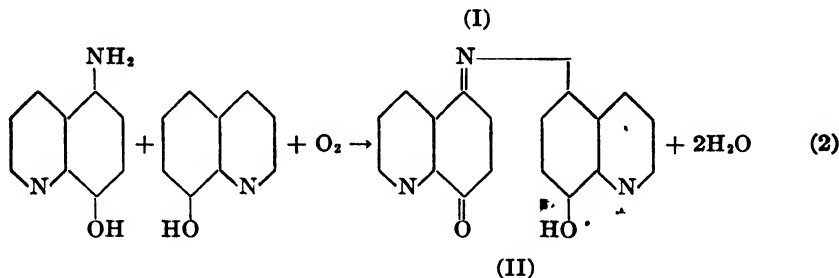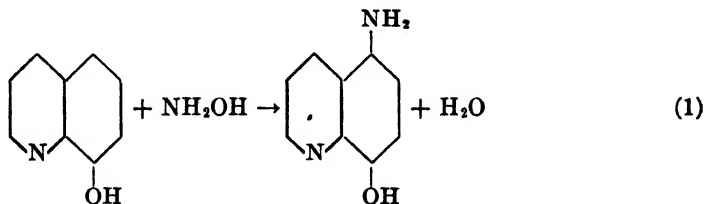
The quinoid compound (II), for which Berg (loc. cit.) proposed the name "indoxine,"[313] is an acid dye with indicator properties. Its alkaline solution, in which the OH group is salt-forming, is green. The acid solution, in which there is probably addition of acids on the nitrogen atom of the quinone, is red. The change interval is pH 6 to 8. Berg and Becker found that 0.08γ hydroxylamine in 1 ml. (1:12,000,000) can be detected by the formation of the green alkali salt of indoxine, when the foregoing reactions are carried out in sodium carbonate solution. Since oxidation is essential to the production of the indoxine, reducing

[311a] J. Hoste, Anal. Chim. Acta. 2, 402 (1948) found that diaminokenzidine reacts in an analogous manner.

[312] R. Berg and E. Becker, Ber. 73, 172 (1940).

[313] This designation is appropriate in view of the constitutional similarity, and also analogy in the (oxidative) method of formation, with the quinoidal indamine and indophenols (quinone-imine dyes) which contain the chromophoric grouping
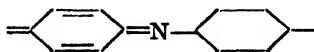
agents, such as hydrazine, should not be present.   Likewise, metal ions that produce insoluble oxinates interfere.   Since most metal ions can be easily separated from hydroxylamine by treatment with sodium carbonate solution, this test can still be regarded as highly selective.   The reaction product of this hydroxylamine test can be isolated quite readily; as a colored derivative of hydroxyquinoline it may be used for various analytical purposes (see p. 191).

Condensation Reactions of Organic Hydroxy Compounds with Boric Acid

Boric acid exhibits a greater tendency to enter into condensation reactions than any other inorganic compound.   This is shown in its behavior toward alcohols and phenols.   The tribasic boric acid is totally or partially esterified; in addition, as will be discussed presently, complex binding exists in certain alcohols and phenol esters.   The most familiar esterifications of boric acid are with the lower monohydric alcohols; the products are volatile esters of orthoboric acid.   The methyl ester (b.p. 65°C.) is formed by warming borates with methyl alcohol, in the presence of concentrated sulfuric acid:

$$H_3BO_3 + 3CH_3OH \rightleftharpoons B(OCH_3)_3 + 3H_2O$$

or more correctly

$$HBO_2 + 3CH_3OH \rightleftharpoons B(OCH_3)_3 + 2H_2O.$$
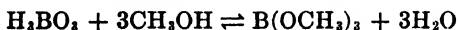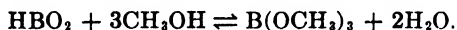
The volatile ester is removed from the saponification equilibrium, and the continuous regeneration of the ester eventually consumes all the boric acid.   The familiar ester or flame test for boric acid is based on the fact that the ester undergoes thermal decomposition to finely divided B_2O_3, which colors a flame green.   Ethyl alcohol can be similarly used; the ester (b.p. 120°C.) evolves along with the alcohol vapors.   The volatilization of $B(OCH_3)_3$ is utilized in the quantitative separation and determination of boron.   The ester can be isolated from the reaction mixture, saponified, and the resulting boric acid carried through a gravimetric or titrimetric procedure.

Esterification of boric acid is involved in the color changes that are observed when colored solutions of polyhydroxyanthraquinones in concentrated sulfuric acid are treated with boric acid.   These color reactions have been used to identify hydroxyanthraquinones.[314]   Feigl and Krumholz[315] showed that sensitive spot tests for boric acid are also possible if very dilute solutions of hydroxyanthraquinones in concentrated sulfuric acid are used as reagents.   Examples of such color reactions, with their respective identification limits are:

[314] J. HOUBEN, *Das Anthrazen und die Anthrachinone*, p. 343.   Leipzig, 1929.
[315] F. FEIGL and P. KRUMHOLZ, *Mikrochemie, Pregl Festschrift*, **1929**, p. 77.

Alizarin S (1,2-dihydroxyanthraquinone-3-sulfonic acid): red yellow → red.. 0.10γ B
Purpurin (1,2,4-trihydroxyanthraquinone): orange → wine red........... . 0.06γ B
Quinalizarin (1,2,5,8-tetrahydroxyanthraquinone):...violet → blue. .   ... 0.06γ B

These color reactions probably do not involve the production of normal phenol esters; it is very likely that inner complex phenol esters are formed. The formation of such inner complex esters between hydroxyanthraquinones and boroacetic acid has been described in a paper that has become one of the classics in complex chemistry. In this study, Dimroth and Faust[316] isolated the colored esters and tested the behavior of isomeric polyhydroxyanthraquinones. They proved conclusively that boroacetic acid only esterifies those OH groups of hydroxyanthroquinones which are in the *peri* position with respect to a CO group. This argues for a direct participation of the CO group in the formation of the ester through coordination on the boron atom. Inner complex esters, such as shown by (I), are formed. It is assumed that analogous inner complex esters are produced in the foregoing color reactions of polyhydroxyanthraquinones with boric acid. For instance, (II) or (IIa) is formed by alizarin S. In (IIa) the likely assumption is made that boric acid in concentrated sulfuric functions as metaboric acid.[317] As yet, there is no direct experimental evidence of these structures as compounds of the types (II) and (IIa) have not been isolated.
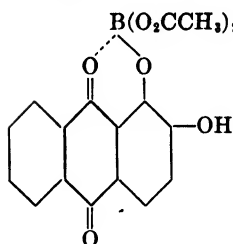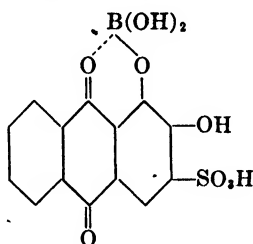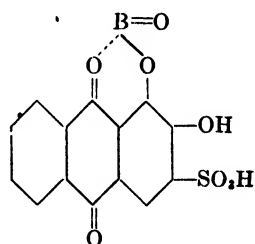
(I)   (II)   (IIa)

Komarowsky and Poluektoff[318] showed that the addition of boric acid causes the blue-violet solution of *p*-nitrobenzeneazochromotropic acid (III) in concentrated sulfuric acid to turn greenish-blue. This characteristic color change, used as a spot reaction, will reveal as little as 0.8γ boron. It should be noted that this reagent is not an hydroxyanthraquinone but an azo compound. Though experimental substantiation is not available, it is quite likely that in this instance, likewise, an inner

[316] O. DIMROTH and TH. FAUST, *Ber.* **54**, 3020 (1921).

[317] O. DIMROTH and TH. FAUST (*loc. cit.*) heated 1-hydroxyanthraquinoneboroacetic ester *in vacuo;* its constitution is analogous to (I). They obtained 1-hydroxyanthraquinone-metaboroacetic ester, corresponding to (IIa).

[318] A. S. KOMAROWSKY and N. S. POLUEKTOFF, *Mikrochemie* **14**, 317 (1933–34).

complex ester is formed, with coordination of the boron atom on one of the nitrogen atoms of the azo group as shown in (IV):

(III)   (IV)
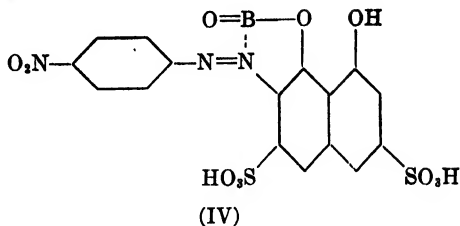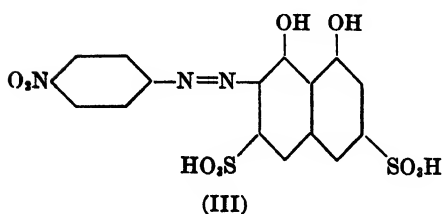
The isolation of a boroacetic ester of p-nitrobenzeneazochromotropic acid would have considerable interest, and would serve to support the assumption that inner complex esters of boric acid are formed. Likewise, the proof that compounds with OH groups in the 1,3-position with respect to the azo nitrogen form no esters would be helpful. In any case, other polyhydroxyanthraquinones and other azo compounds with OH groups in coordination positions relative to CO or —N==N groups will doubtless be found to function as color reagents for boric acid in concentrated sulfuric acid solution.

The foregoing esterifying reactions of boric acid proceed only in the presence of concentrated sulfuric acid as condensing agent. (Possibly syrupy phosphoric acid could be used.) However, another class of condensation reactions, in which boric acid condenses with aliphatic and aromatic hydroxyl compounds, proceed without the addition of a dehydrating agent. These reactions occur at room temperature and with an excess of the hydroxyl compound dissolved in water. No characteristic color changes result, but the incorporation of the boric acid into the hydroxyl compound leads to "activation" of the boric acid (see Chapter V). This activation, which is more correctly designated as increased acidification of the reaction system, finds important application in certain analytical procedures. Thompson[319] seems to have been the first to make analytical use of the activation of boric acid by glycerol, although the effect was reported by Biot[320] more than half a century earlier. When glycerol is added to the aqueous solution, the very weak boric acid becomes so strong a monobasic acid that its alkali salts no longer hydrolyze. Consequently, it is then possible to titrate boric acid sharply with alkali hydroxide, in the presence of phenolphthalein as indicator. Later, it was discovered that other polyhydric alcohols, such as mannitol and invert sugar, also act as activators for boric acid. The increased acidity of aqueous boric acid solutions is connected with an increased conduc-

[319] R. T. Thompson, *J. Soc. Chem. Ind. (London)* **12**, 432 (1893).

[320] J. Biot, *Compt. rend.* **14**, 49 (1842).

tivity. Such conductance measurements were first made by Magnanini.[321] He concluded from the relation between the conductivity and the ratios B_2O_3: polyhydric alcohol (dulcitol, mannitol, erythritol, glycerol) and the respective dilution, that complexes are formed. More intimate insights into the chemical basis of the activation of boric acid were given by the fundamental studies of Böeseken.[322] He proved that certain group actions play a role. He investigated also the behavior of aromatic hydroxyl compounds (phenols and hydroxyanthraquinones). Among other facts, he discovered the important point that, of the three dihydroxybenzenes, only pyrocatechol confers a strongly increased conductance on water solutions of boric acid, while among the three trihydroxybenzenes both pyrogallol and hydroxyhydroquinone are active. The activating di- and trihydroxybenzenes have two OH groups on carbon atoms that are directly bound to each other. However, this in itself is obviously not sufficient to bring about the increase in conductivity, since glycol, $HO—CH_2—CH_2—OH$, has no effect on the strength of boric acid. Böeseken concluded that an increased conductivity is secured if, as in the polyhydric phenols just cited, the OH groups are attached to adjacent carbon atoms on the same side, so that a ring system, such as

$$\begin{matrix} C—O \\ | \quad\quad\ B—OH \\ C—O \end{matrix}$$
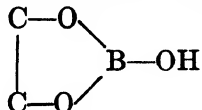
is possible. In glycol, the two OH groups are free to rotate about the bond connecting the two carbon atoms, and consequently

$$\begin{matrix} HO—CH_2 \\ | \\ H_2C—OH \end{matrix}$$

seems to be the preferred configuration.
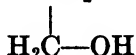
Accordingly, all of the activating polyhydric alcohols (mannitol, erythritol, dulcitol, sorbitol, as well as glycerol) must have at least two OH groups in the position corresponding to that in the activating phenols, *etc.* Hence the increased acidity of boric acid brought about by polyhydric alcohols, and evidenced by conductance measurements or indicators, has become an aid in determining the configuration of these alcohols. The studies of Böeseken lead to the assumption that at least the first stage in the enhancement of the acidity of boric acid by aliphatic and aromatic polyhydroxy compounds is due to the initial formation of a diester boric acid. This condensation is shown schematically in (1). A second condensation (2) may then lead to the production of an acid whose anion contains inner complexly linked boron:

[321] G. MAGNANINI, *Z. physik. Chem.* **6**, 68 (1890).

[322] J. BÖESEKEN and collaborators. Their papers can be found mostly in *Rec. trav. chim.* from 1921 to 1930.

$$
\begin{array}{c}
\diagdown \\
\diagup
\end{array}\!\!C\!\!-\!\!OH \quad HO\diagdown B\!\!-\!\!OH \xrightarrow{-2H_2O} \begin{array}{c}\diagdown\\\diagup\end{array}\!\!C\!\!-\!\!O\diagdown B\!\!-\!\!OH \rightleftharpoons \begin{array}{c}\diagdown\\\diagup\end{array}\!\!C\!\!-\!\!O\diagdown B\!\!-\!\!O^- + H^+ \quad (1)
$$

$$
\begin{array}{c}\diagdown\\\diagup\end{array}\!\!C\!\!-\!\!O\diagdown B\!\!-\!\!OH + HO\!\!-\!\!C\diagup \xrightarrow{-H_2O} \left[\begin{array}{c}\diagdown\\\diagup\end{array}\!\!C\!\!-\!\!O\diagdown B\diagup O\!\!-\!\!C\diagdown \right]^- + H^+ \quad (2)
$$
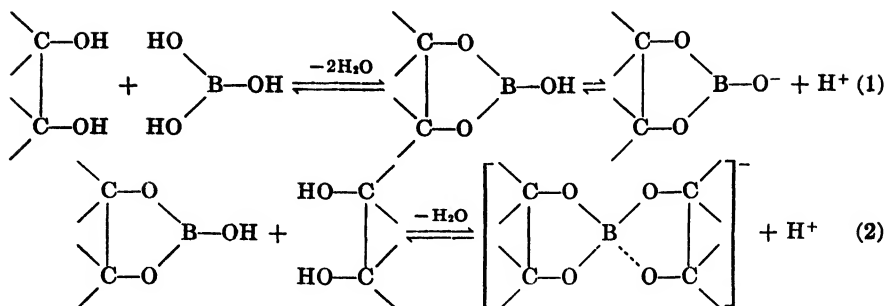
There are evidences supporting the possibility of (1) as well as (2). Fox and Gauge[323] isolated a mannitolboric acid and some of its salts, in which the ratio of boron to mannitol is 1:1, as demanded by a condensation like that shown in (1). On the other hand, Neuberg and Wohl[324] isolated a potassium salt of a glycerol-boric acid in which the ratio is 1B:2 glycerol. Böeseken and Meulenhoff[325] isolated salts of a dipyrocatecholboric acid. The structure

$$
\left[\bigcirc\!\!\begin{array}{c}-O\\-O\end{array}\!\!B\!\!\begin{array}{c}O-\\O-\end{array}\!\!\bigcirc\right] HR
$$

R = ammonia, aniline, p-chloroaniline, dimethyl-aniline, pyridine
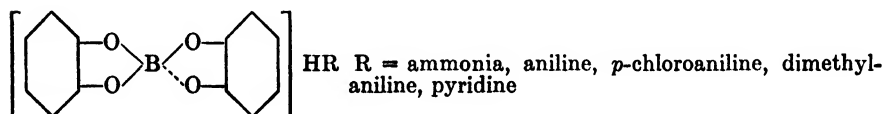
likewise corresponds to the occurrence of a condensation as shown in (2). It should be noted that the isolation of salts of a dipyrocatecholboric acid from a solution of the components merely indicates that this acid is formed, but this should not be taken as a conclusive proof that this acid is the sole cause of the increased acidity. Reactions (1) and (2) may proceed concurrently; they both lead to monobasic acids. Analogous considerations apply to polyhydric alcohols.

A definite decision whether the reactions proceed according to (1) or (2) is not of decisive significance with respect to the analytical effect of adjacent OH groups in organic compounds to produce an enhanced acidity of boric acid, nor with respect to the classification of this interesting phenomenon under condensation reactions. However, a sure decision is important as to the correct term to be used for the mutual action between boric acid and polyhydroxy compounds. Obviously, the term "activation of boric acid" is appropriate only for the production of compounds of the type shown in (1), because here one of the three OH groups of the boric acid has been preserved. In contrast, none of the OH groups of the boric acid is still present in the complex acids of the

[323] J. J. Fox and A. J. H. Gauge, J. Chem. Soc. 99, 1075 (1911).
[324] C. Neuberg and A. Wohl, Ber. 32, 3488 (1899).
[325] J. Böeseken and J. Meulenhoff, Chem. Abstracts 18, 1988 (1924).

type produced according to (2). In the case of the pyrocatechol compound the enhanced acidity applies only to the weakly acid pyrocatechol, and in truth it and not the boric acid is activated. The author believes that complex formation is more likely with aromatic polyhydroxy compounds, and that this will proceed to a greater extent than with aliphatic polyhydroxy compounds.

The studies of Krautz and his coworkers[326] are interesting with respect to the activation of boric acid by polyhydric alcohols. They showed that in the series:

Ethylene glycol	Glycerol	Erythritol	Adonitol	Mannitol (dulcitol, sorbitol)
CH_2OH	CH_2OH	CH_2OH	CH_2OH	CH_2OH
CH_2OH	$CHOH$	$(CHOH)_2$	$(CHOH)_3$	$(CHOH)_4$
(no reaction)	CH_2OH	CH_2OH	CH_2OH	CH_2OH

the acidity-enhancing influence of the polyhydric alcohols rises with increasing number of carbon atoms and OH groups in the molecule. Their anhydrides have a weaker action than the corresponding alcohols. A striking exception is erythritan, $CH_2—CH(OH)—CH(OH)—CH_2$, derived from

erythritol; its action exceeds that of mannitol. This finding can be taken as a nice proof that the inactivity of ethylene glycol is not due to its having too few OH groups but, as Böeseken assumes, to the steric configuration of the two OH groups (see p. 357).

With reference again to the analytical utilization of the increased acidity in the system: boric acid + polyhydric alcohol, it should be noted that the condensation reactions as shown in (1) and (2) are equilibrium reactions. Consequently, the acidity, for a given hydroxy compound, depends on the quantity and concentration of the reactants, and on the temperature. For example, with mannitol, which is the most commonly used activator of boric acid, the acidity of the mixture decreases with rising temperature and greater dilution, because the mannitol-boric acid is decomposed by these factors. Conversely, a solution of boric acid, at a given temperature and concentration, becomes increasingly acidic as more and more mannitol is introduced, since the equilibrium is thus shifted toward the right. The acidity of 0.1 M boric acid that contains 4 moles of mannitol per mole of boric acid is equal to that of 0.1 M acetic acid.

The enhancement of the acidity of boric acid by polyhydric alcohols was applied, for many years, solely in the titrimetric determination of boric acid. Hahn[327] developed a specific test for boron based on the

[326] J. C. KRAUTZ, M. OAKLEY and C. J. CARR, J. Phys. Chem. 40, 151, 927 (1936).
[327] F. L. HAHN, Compt. rend. 197, 762 (1933).

increase in acidity obtained in the boric acid-mannitol system. In this procedure, isoalkaline solutions of mannitol and of the material to be tested for boric acid are brought together, with bromthymol blue as indicator. As little as 0.02γ boron in 1 ml. is revealed by the change from green to yellow. As a spot reaction, the limit is 0.001γ boron. These identification limits, as well as the corresponding concentration limit (1:50,000,000), show that this is not only the most sensitive test for boron, but it is, in fact, one of the most sensitive of all known tests.

The turmeric test for boric acid gives a change from yellow to red in the presence of mineral acids; on alkalization the color turns to blue. The chemistry of this familiar reaction has not been completely elucidated.[328] It is only known that the red-brown rosocyanin,[329] the end-product of the reaction, contains no boron. Possibly, there is an intermediate esterification by boric acid of the alcoholic or phenolic OH groups, and also a production of a complex. Inspection of the structural formulas of curcumin (I), which is the coloring principle of turmeric (curcuma), and of its enolization product (II), shows that esterifiable OH groups are present, and that they occupy positions permitting coordination with CO and OCH_3 groups, respectively:
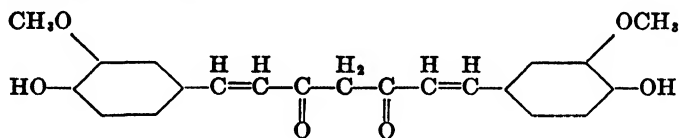
(I)
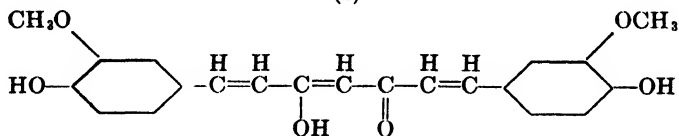
(II)

The increased acidity, occasioned by bringing boric acid and polyhydroxy compounds together in aqueous solution, is highly selective for boric acid, but it is not strictly specific. Rosenheim and Weinheber[330] found that weak telluric acid is activated by glycerol. Similarly, Tschakirian[331] observed that germanium dioxide plus glycerol, glucose, or mannitol, forms a strong monobasic acid, which, according to Poluektoff,[332] can be satisfactorily titrated with bases, in the presence of phenol-

[328] For literature on the boric acid-turmeric reaction see E. M. CHAMOT and H. J. COLE, *Ind. Eng. Chem.* **10,** 48 (1918).

[329] M. E. SCHLUMBERGER, *Bull. soc. chim.* [2] **5,** 194 (1866).

[330] A. ROSENHEIM and A. WEINHEBER, *Z. anorg. allgem. Chem.* **69,** 266 (1911).

[331] A. TSCHAKIRIAN, *Compt. rend.* **187,** 229 (1928).

[332] N. S. POLUEKTOFF, *Z. anal. Chem.* **105,** 24 (1936).

phthalein. Studies by Tschakirian[333] show that the activation by mannitol in the presence of strong electrolytes (*e.g.*, $CaCl_2$) goes so far that H_2GeO_3 functions as a dibasic acid. No study has been made to learn whether these activations involve processes similar to those operative with boric acid. It is entirely possible that, in these cases also, a role is played by condensation reactions between alcoholic OH groups and GeO_2 or TeO_3. Favoring evidence is the fact that germanicacid behaves toward polyhydroxyanthraquinones as boric acid does; for instance, it can form colored esters.[334] However, the detection of the production of these esters is not nearly so sensitive as in the case of boric acid.

Condensation Reactions of Pyrocatechol with Hydroxides of Metals and Nonmetals

The preceding section, which dealt with the activation of boric acid as a consequence of its condensation reactions with various organic hydroxy compounds, contained a reference (p. 358) to its condensation with pyrocatechol to produce dipyrocatecholboric acid. It is interesting that pyrocatechol undergoes analogous condensation reactions with certain other oxygen acids, *i.e.*, with hydroxides of nonmetals, and also with many metal hydroxides. The products are pyrocatechol complex salts, many of them being quite stable. The chief sources of information regarding the formation and composition of the pyrocatechol complexes with 2-, 3-, and 4-valent metals, as well as with metal acids are the numerous studies by R. Weinland, also by A. Rosenheim, and later by H. Reihlen.[335]

In the metal pyrocatechol compounds, the hydrogens of the OH groups have been replaced by metal atoms and compounds with inner complex anions result. The following coordination formulas represent the most important types of these salts of 2- to 4-valent metals:

2-valent metals
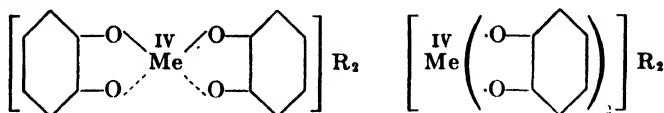
3-valent metals
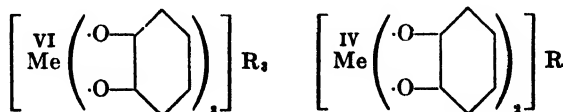
[333] A. Tschakirian, *Bull. soc. chim.* [5] **10**, 98 (1943).

[334] N. S. Poluektoff, *Mikrochemie* **18**, 48 (1935).

[335] Compare P. Peiffer, Organische Molekülverbindungen, pp. 334*ff*. Stuttgart, 1927.

4-valent metals

$$\left[\begin{matrix} \text{VIII} \\ \text{Me} \end{matrix} \left(\cdot\text{O} \!\!-\!\!\!\! \bigcirc \!\!\!\!-\!\! \cdot\text{O} \right)_4 \right] R_4 \qquad \left[\begin{matrix} \text{VI} \\ \text{Me} \end{matrix} \left(\cdot\text{O} \!\!-\!\!\!\! \bigcirc \!\!\!\!-\!\! \cdot\text{O} \right)_3 \right] R_2$$
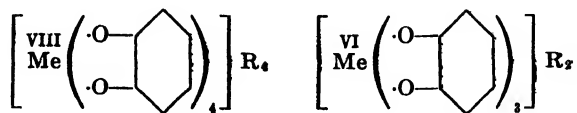
(IV, VI, and VIII signify the coordination numbers of the metal atoms in the complexes; R = H, NH₄, pyridine, alkali metal atom, *etc.*)

The foregoing compounds result from the condensation of metal hydroxides with pyrocatechol. This is clearly proved by the fact, for instance, that the water-soluble ammonium salts of these complexes are produced by digesting the respective metal hydroxide with an ammoniacal solution of pyrocatechol:

$$Me(OH)_2 + 2C_6H_4(OH)_2 + 2NH_3 \rightarrow (NH_4)_2 \left[Me \left(\begin{matrix} \cdot O \\ \cdot O \end{matrix} \diagdown C_6H_4 \right)_2 \right] + 2H_2O$$
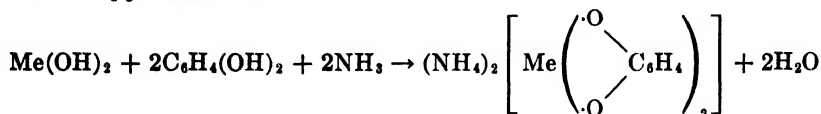
The alkali salts can be prepared analogously, *i.e.*, by digesting metal hydroxides with alkaline solutions of pyrocatechol.

This method of producing the ammonium salts of the pyrocatechol complexes is particularly interesting in view of the fact that ammonium salts of pyrocatechol do not exist. As a phenol, the latter is a very weak acid and hence has but slight salt-forming properties. Its acidic character and salt-forming abilities are increased only after metal atoms are incorporated in the pyrocatechol molecule. Hence, the effect is logically termed "activation of pyrocatechol."

When a quantity of pyrocatechol slightly in excess of the amount demanded by the equation is used to dissolve a metal hydroxide, the dissolution becomes less complete the older the metal hydroxide.[336] Correspondingly, the stoichiometric quantity of pyrocatechol dissolves the hydroxide quickly and completely provided the latter is presented in *statu nascendi*, *i.e.*, if a solution of the metal salt is mixed with pyrocatechol and then treated with alkali. It may be assumed that, under

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[336] If, for example, an aqueous solution containing an aluminum salt and pyrocatechol in the ratio 1Al:3C₆H₄(OH)₂ is treated with excess ammonia, no precipitate of Al₂O₃·xH₂O results. When the hydrous alumina is precipitated with ammonia and the suspension then immediately treated with pyrocatechol, complete solution occurs. If the aluminum hydroxide is precipitated hot, then cooled, and pyrocatechol added, a considerable fraction of the precipitate remains undissolved. Alumina precipitated at room temperature becomes progressively less soluble in pyrocatechol the longer it is aged in the ammoniacal medium. Other metal hydroxides that can condense with pyrocatechol appear to behave similarly. There is some possibility that aging processes of hydrous metal oxides can be followed and compared by determining the extent of the formation of the pyrocatecholate. (Unpublished observations of the writer.)

such conditions, the metal hydroxide reacts as a colloidal dispersoid, a condition that invariably precedes the formation of a visible precipitate (see Chapter X).

Condensations of pyrocatechol with hydroxides of nonmetals will be exemplified here by tripyrocatecholarsenic acid. It is formed from arsenic acid and pyrocatechol:
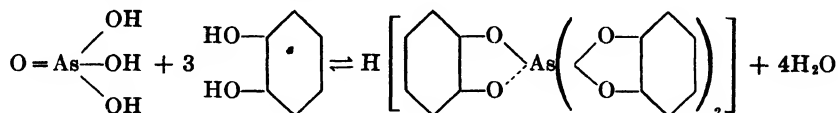
The solid acid is easily isolated; in dilute solutions it gradually suffers partial hydrolysis into its components. The salts are stable; some of them are difficultly soluble in water. The acid has found use as a sensitive precipitant for certain alkaloids.[337] For example, quinine can be detected in 0.002% solution.

A consideration of the behavior of pyrocatechol may not, at first glance, appear germane to a study of the specific and selective actions of certain atom groupings in organic compounds. However, this material condenses with the hydroxides of numerous metals and non-metals; in fact, pyrocatechol complexes of 21 elements are now known, some in various valence states. Consequently, there can be no question of selectivity. If the behavior of pyrocatechol is none the less discussed here, the justification lies in the fact that there is every likelihood for the development of selective precipitation reactions based on the ease with which pyrocatechol complexes are formed. No hydroxide precipitation occurs in solutions of the pyrocatechol complexes of di- to quadrivalent metals, *i.e.*, the pyrocatechol functions as a masking agent. This does not mean that it will prevent all other precipitation reactions. A quantitative precipitation of a compound, whose solubility product is less than that of the corresponding hydroxide, is entirely possible; the same reasoning will apply to color reactions. Experiments along these lines have not been made. Furthermore, the precipitation of alkaloids by tripyrocatecholarsenic acid points toward still other precipitating actions. In fact, it was observed[336a] that this complex acid, as well as several ammonium salts of metal pyrocatechol complexes, give red precipitates in aqueous ammoniacal solution with ferrodipyridyl sulfate, which is a good reagent for precipitating complex anions.

Selective Behavior of Disodium-1,2-Dihydroxybenzene-3,5-Disulfonate

Among the metal-pyrocatechol compounds mentioned in the preceding section, the colored ferric salts are closely related to the products

[336a] F. FEIGL, unpublished studies.

[337] R. WEINLAND and J. HEINZLER, *Süddeuts. Apoth. Ztg.* 61, 46 (1921).

of an iron reaction with a disulfonated pyrocatechol. Yoe and Jones[338] found that disodium-1,2-dihydroxybenzene-3,5-disulfonate gives a blue color with ferric ions at pH 4–5. On the addition of alkali (pH 5.7–6.5) the color goes toward violet, and above pH 7 it changes to red. These color reactions are exceedingly sensitive. When carried out as a spot reaction, the detection limit is 0.05γ Fe (1:1,000,000). When viewed through longer layers (in a Nessler tube) the blue or the red coloration will reveal the iron at dilutions of 1:30,000,000 and 1:200,000,000, respectively. This great sensitivity is due to the production of compounds with very small ion products, since the color reaction is not prevented by typical masking agents for iron (fluoride, phosphate). Furthermore, the conditions required for a very extensive selectivity are easily established, since only cupric and thallic ions produce colored, soluble compounds with this reagent. Hence, it is a very valuable tool for the detection and colorimetric determination of iron.

A critical consideration of the assumptions of Yoe and Jones regarding the composition and constitution of the colored ferric compounds of the reagent recommended by them lead to interesting perspectives. They correctly seek a relationship with the blue and red ferric pyrocatechol compounds isolated by Reihlen[339] and by Weinland and Walter.[340] These compounds contain inner complex anions, which differ in their respective iron:pyrocatechol ratios as shown by the structures:

blue   red
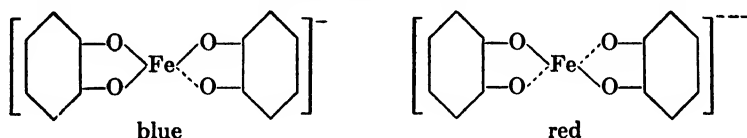
Yoe and Jones believe that the coordination formulas I–III should be given serious consideration for the iron compounds of the disulfonated pyrocatechol. The present writer, however, thinks that the coordination theory lends more likelihood to the adjacent formulas I*–III*.

A definite decision between these structures cannot be made now because the various compounds have not been isolated. However, the following considerations make it quite clear that a question of fundamental importance is involved. The formulas I–III state that the SO_3Na groups, which, according to all previous experience, are ionizable, have lost their dissociability by being incorporated in the complex anion. The formulas I*–III* stipulate the presence of abnormal highly charged anions. In the first case, as well as in the second, complex types of

[338] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.* **16**, 111 (1944).
[339] H. Reihlen, *Z. anorg. allgem. Chem.* **123**, 173 (1922).
[340] R. Weinland and E. Walter, *Z. anorg. allgem. Chem.* **126**, 148 (1923).

binding are involved, which merit great interest with respect to the constitution of polysulfonated (possibly also polycarboxylated) derivatives of organic complex-formers. It is entirely proper to raise the question as to whether the alkali and other salts of such compounds are actually capable of existence in the solid state, and, hence, isolable. It is quite difficult to picture how it is possible for molecules or ions of such compounds to arrange themselves in a solid crystal lattice. Perhaps these compounds are representatives of a type of combination that can exist only in solution. This is far from being a wild notion. There are many complex compounds that are stable only in melts, and many

Blue Ferric Pyrocatecholdisulfonate

Violet Ferric Pyrocatecholdisulfonate

Red Ferric Pyrocatecholdisulfonate
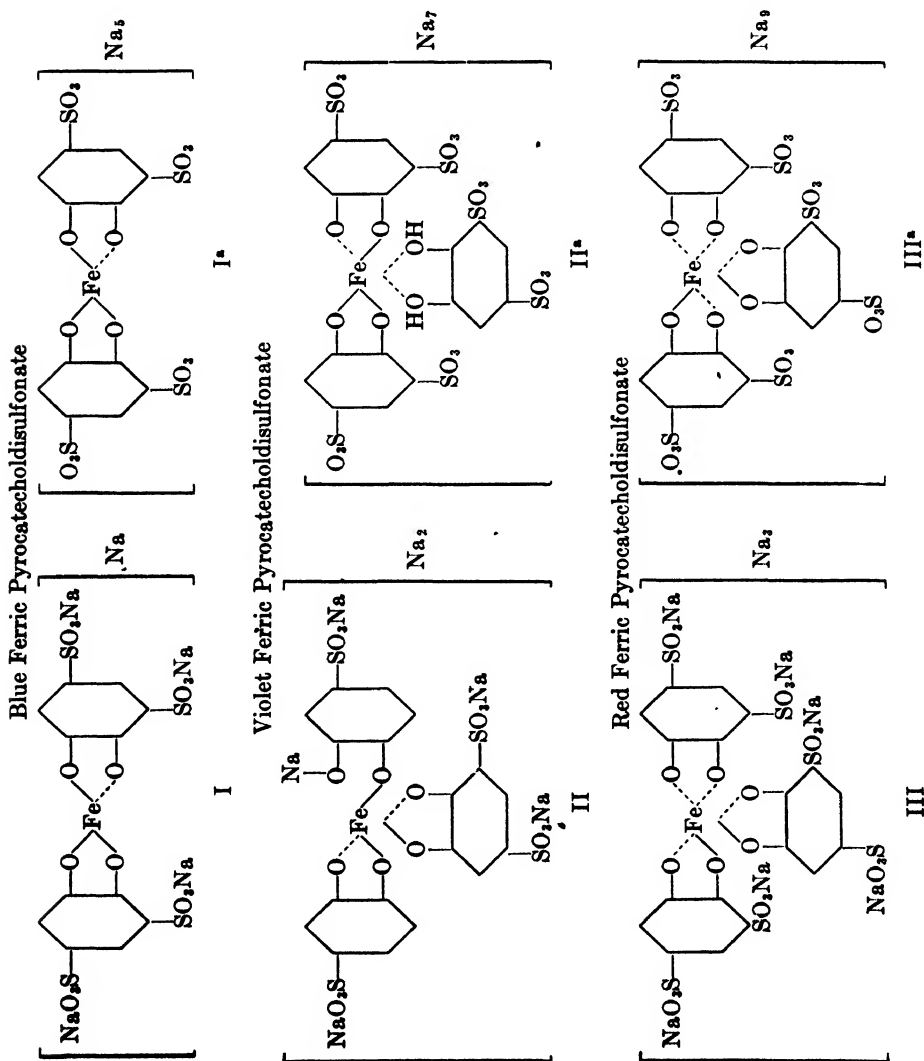
instances can be cited from the much more simply constructed hydrates of metal salts that a hydration, which has been amply proven to exist in solution, is not retained in the solid crystalline form.

Other facts fundamental to complex chemistry can be pointed out. The coordination formulas for the blue ferric salts of pyrocatechol and its sulfonated derivative show that, despite the inner complex binding, the iron atom is not saturated. A further inner complex binding is possible with an increase in the coordination number. The erroneous notion that inner complex binding invariably is coincident with coordinative saturation was disputed in the discussion of insoluble complex salts of 8-hydroxyquinoline and quinaldic acid (see pp. 184, 322). It is now apparent that this notion can not hold in its general form for soluble inner complex compounds either. A comparison of the red and blue ferric compounds of pyrocatecholdisulfonic acid demonstrates, furthermore that an increase in the number of the inner complex rings in the molecule of the compounds is accompanied by an intensification of the color. This is probably the reason for the enhanced sensitivity found by Yoe and Jones in the detection of iron by means of the red compound with pyrocatecholdisulfonic acid. The great sensitivity and certainty of the Yoe-Jones reaction indicates that the stability of the resulting compounds is undoubtedly greater than that of the corresponding pyrocatechol compounds. It might be thought that SO_3H groups, which strengthen the electrolytic character of the pyrocatechol, would lessen the tendency toward incorporation in an inner complex anion. Precisely the opposite is the case. The instances discussed in this section again prove the important point that analytical effects can form the basis of trains of thought which may lead into other special provinces of chemistry.

The Formation of Thioketone with Free Sulfur

Schönberg and Urban[341] showed that free sulfur reacts with benzyl-imido-di(4-methoxyphenyl)-methane (I) to form p,p'-dianisylthioketone (II). The reaction occurs if a mixture of (I) and sulfur, or a product containing free sulfur, is kept for several minutes at 210°C. They represent the reaction:

$$C_6H_5-CH_2-N=C \begin{matrix} C_6H_4OCH_3 \\ \\ C_6H_4OCH_3 \end{matrix} \quad + S \rightarrow \quad S=C \begin{matrix} C_6H_4OCH_3 \\ \\ C_6H_4OCH_3 \end{matrix}$$

<div align="center">(I)   (II)</div>
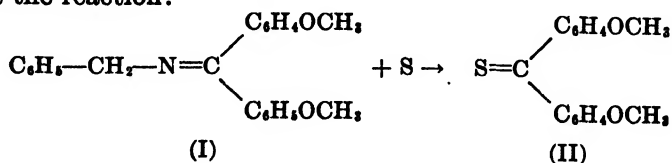
but this gives no information regarding the nature of the nitrogenous compounds that are formed at the same time. It seems reasonable to

[341] A. Schönberg and W. Urban, *Ber.* 67, 1999 (1934).

assume that the reaction takes the following course.   At the elevated temperature, the double bond between nitrogen and carbon in the group

$$-N{=}C{<}^{Ar}_{Ar}$$ (Ar = aryl) is loosened to such·an extent that partial
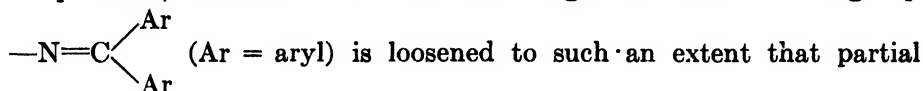
dissociation into free radicals follows.   The addition of sulfur to the radical containing divalent carbon then leads to the formation of the thioketone.   If this postulate is valid, other compounds with structures analogous to (I) ought also to give similar reactions with sulfur at higher temperatures.   There seem to be no available studies of the question as to whether sulfur will likewise add to the radical containing nitrogen. Any production of the thioketone is revealed by the green solution that is obtained when the melt is extracted with benzene.   The green color is discharged if a small crystal of mercuric chloride is added.   The surface of the crystal acquires a red coating, due to the addition compound $HgCl_2 \cdot SC(C_6H_4OCH_3)_2$.

The fusion reaction required to form the thioketone can be carried out in a capillary tube.   In this form, the test may be used for the detection of minute quantities of sulfur.   The tube is crushed, and the reaction product is taken up in warm benzene.   As little as 40γ free sulfur can be detected with certainty by means of the green color of the solution or through the formation of the red mercuric chloride addition compound. It is not known whether the procedure can be applied to the quantitative (colorimetric) determination of sulfur.

This color reaction has considerable analytical significance.   It is the first direct test for free sulfur.   Formerly, it was necessary to extract the suspected sample with carbon disulfide; a questionable expedient since amorphous sulfur does not. dissolve in this liquid.   The new test has the additional advantage of being strictly specific, as sulfur in organic or inorganic combination does not react.   Likewise, free or combined selenium is inactive.   This fusion reaction, therefore, makes it possible to determine whether or not sulfur-bearing compounds split off free sulfur at or below the temperature employed in this procedure.   The originators of this test found that a number of organic disulfides withstand such heat-treatment.[342]

In the past, the discoverers of this type of reaction, which is of great

[342] A red precipitate is obtained from the reaction: $2H_2S + H_2SeO_3 \rightarrow 3H_2O + Se + 2S$.   It would be interesting to learn, with the aid of the above test, whether this precipitate is selenium disulfide or a mixture of sulfur and selenium.   In case a temperature-resistant SeS_2 is formed, no reaction, or a weakened sulfur reaction, may be expected.   The failure of the catalyzed iodine-azide test (see page 126) for sulfides, is taken by the author as proof of the presence of a sulfur-selenium mixture produced by the preceding redox reaction.

importance to the chemistry of free organic radicals, would hardly have given a thought to using it for analytical purposes. Its application in this field is a welcome indication that the objectives propagated by the author are gaining ground. His creed is: the solution of micro-analytical problems should draw upon every technique and every type of reaction that gives promise of producing extensive selectivity and sensitivity.

Effect of Certain Atomic Groupings on the Specific and Selective Activity of Compounds in Organic Analysis

The immense number and great variety of organic compounds would present a vast chaos of materials if it were not possible to arrange them in classes. The members of each class are characterized by containing certain atomic groups. These groups are not only the basis of the systematic classification of organic compounds, they also determine, in many cases, the physical and chemical properties of the materials of which they are a part. Consequently, all the chemical processes of organic analysis and, therefore, also the unequivocality and sensitivity of tests rest on the reaction capability of certain atomic groups. Quite often this reactivity differs decidedly from that shown by the inorganic compounds employed in qualitative and quantitative procedures. In fact, a really analogous reaction mechanism is encountered in the two great divisions only when acidic or basic groups produce a salt. Even in such cases, normal salts are produced less often with organic reagents than inner complex salts and other kinds of complex compounds. With many organic groups, the mechanism of test reactions consists of condensation or degradation processes, or of redox reactions, that are applied to either the solid sample or to its solution, usually in an organic liquid. Such processes, which at times are simply steps preliminary to the actual analytical tests, are ordinarily not ionic but rather molecular reactions. Their velocity is sometimes low, and often they do not go to completion.[1] A fundamental difference in the reaction ability of inorganic and organic atomic groups lies in the fact that the former, when present as ions, or as the ionic dissociation products of slightly soluble

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[1] This should not be taken as stating that, in general, all molecular reactions proceed more slowly than ionic ones. H. KAHLENBERG and his school [compare *J. Phys. Chem.* 6, 1 (1902)] showed that numerous precipitations, such as metatheses of metal oleates with H_2S, proceed just as rapidly in hydrocarbons as the corresponding ionic reactions in aqueous solution. The dissolved and reacting molecules of metal oleates in benzene solutions, which are nonconductors, are not simple but polymerized. Furthermore, reactions in concentrated aqueous solutions, and reactions of slightly dissociated compounds in aqueous solutions, are also in part molecular reactions [compare F. HABER, *Z. Elektrochem.* 10, 773 (1904)]. The domain of slow reactions at higher concentrations of the reactants includes changes that do not result in the formation of a salt, but lead to an exchange, or to definite alterations in the atomic groups of the molecule of a compound. Such exchanges and alterations are encountered particularly in organic preparative work, and the statement in the text refers to them.

compounds, invariably react in a way that is characteristic of the particular ionic species. Such distinctive action is not always shown by organic atomic groups. The latter are never independent constituents of the whole molecule of which they form a part. Hence, organic analysis constantly presents the fact, repeatedly emphasized in Chapter VI, that organic compounds, even though they contain the same groups, do not always react alike with a given reagent. Other groups, which take no direct part in the real group reaction, often exert a determining effect on the reaction capability of the entire molecule. This influence extends to the reaction velocity which, in some cases, is so reduced that the material is practically unreactive.[2] Frequently, this influence is reflected also in the color and solubility of the reaction products. The effect is so marked in some cases that the same group reacts in entirely different ways with the same reagents. A familiar example is the divergent behavior of primary aliphatic and aromatic amines toward nitrous acid.

It is important to point out the difference in the reaction capability of inorganic and organic groups, because this difference confers a meaning on the concepts "specificity" and "selectivity" as applied in organic analysis that is somewhat different from that accepted in inorganic analysis. In the latter field, these terms signify the complete, or the more or less extensive, unequivocality of a reaction or a test applied to materials that are present together. In organic analysis, there is the additional factor of the influence on nonequivocality possibly exerted by other groups contained in the same molecule. Consequently, specific and selective tests for certain groups in organic compounds must be as independent as possible of the rest of the composition and structure of the molecule. Analytical importance, however, attaches also to such group reactions as are influenced in a known way by other groups of the molecule. Information regarding such effects is often gained only by actual trials. When an organic compound is tested, and it gives a positive response to a given group reaction and a negative or modified response to another group reaction, it is often possible to make useful deductions regarding the structure of the compound that has been subjected to the two tests. Hence, differences in the actions of an atomic group toward various reagents can be of real service in revealing the presence of the groups responsible for the deviations from the normal behavior. This point is important with respect to specificity and selectivity of tests in organic analysis.

Qualitative organic analysis is much younger than qualitative

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[2] The interference with the reaction capability of an atomic group exerted by other groups present in the same molecule can be termed an inner molecular irreversible masking. This type of masking is fundamentally different from the always reversible masking of inorganic compounds (compare Chapter IV).

inorganic analysis. Its tasks are usually more varied and more difficult to accomplish, especially when intricately constructed organic compounds are to be identified with certainty. Relatively few purely chemical tests are now available for such assignments. In most instances, absolute identification is only possible by first isolating either the compound itself or a derivative prepared from it, and then determining physical constants, such as melting point, boiling point, *etc.* Sometimes it is also necessary to make a quantitative determination of certain elements or groups. In contrast, that province of qualitative organic analysis which is restricted to the detection of certain typical atomic groups has been much more widely developed and is being constantly extended. The problems of specificity and selectivity, as well as of sensitivity, so constantly emphasized in this book, apply equally to this branch of qualitative organic analysis and to inorganic analysis.

There are many examples which show that the objective of a qualitative organic analysis has been accomplished completely by the identification of certain atomic groups. This is the case when, in preparative organic chemistry, certain steps of a synthesis or degradation of compounds are to be followed through control tests. In other instances, certain constituents of natural or artificial products are to be detected or isolated, or purity tests on organic products are required. But even when an absolute identification of organic compounds is necessary, the proof of the presence of certain groups frequently provides valuable criteria for further chemical and physical tests.

Three fundamentally different categories should be distinguished in the qualitative testing of organic compounds by means of certain group actions. They are:

(1) Preliminary tests based on group actions;
(2) Direct examination for certain atomic groups by reaction with inorganic or organic reagents;
(3) Conversion of organic compounds into products with characteristically reacting atomic groups.

The typical examples cited here to illustrate the three classes were selected because in these cases specific or selective tests are possible even if conducted by the technique of spot analysis. In other words, the procedures used are so sensitive that they succeed with a single drop of test solution, or with minute quantities of the solid sample.

PRELIMINARY TESTS BASED ON GROUP ACTIONS

Directive or preliminary tests are of as great value in qualitative organic analysis as they are in qualitative inorganic analysis, since they often indicate the presence or absence of members of certain large classes

or organic compounds. The course of a systematic examination is thus considerably facilitated and simplified. Practically all, or at least the most important, preliminary tests for organic compounds are based on certain group actions, or on characteristic alterations that atomic linkings undergo in these preliminary tests. Apart from the calcination test designed to detect ignition-resistant constituents in organic compounds, these procedures include the fixation of certain nonmetallic elements (sulfur, phosphorus, arsenic, fluorine, *etc.*) by igniting a portion of the sample after it is mixed with lime or magnesium oxide. Calcium sulfate, phosphate, arsenate, and fluoride, or the corresponding magnesium salts result, *i.e.*, compounds that can easily be identified by the tests used in qualitative inorganic analysis.[3] A group action is most marked when carrying out tests of solubility with inert solvents, or with reaction solvents. Such solubility tests are not only an essential part of preliminary tests, but frequently are also indispensable in the separation of the ingredients of a mixture prior to their identification. It is common practice to make the sample alkaline by adding hydroxide, carbonate, or bicarbonate and then extract with ether. This process serves to liberate and separate basic compounds, which then pass into the ether layer, from acids and phenols, which remain in water solution as alkali salts. The reverse process, namely, extraction of a sample treated with a mineral acid, serves to fix basic compounds as their salts in aqueous solution, and to free from their salts the acidic compounds, which, if ether-soluble, may then pass into the ether layer along with the so-called neutral compounds. Considerable information concerning the class of compounds to which the sample, or parts of it, belong can often be secured by tests of the solubility in water and in various types of organic solvents. An important role is played here by the fact that similarity in constitution or possession of like atomic groups by the molecules of the solute and solvent is often an essential factor in determining solubility (see Chap. VIII).

The ability of certain groups to produce solvates by adding sulfuric acid, acetic anhydride, or dimethyl sulfate, is the basis of the solubility of numerous organic compounds in concentrated sulfuric acid, or in mixtures of sulfuric acid and acetic anhydride (sometimes with production of characteristic colored solutions), and of the solubility of certain aromatic compounds in dimethyl sulfate. Since solvates in sulfuric acid or dimethyl sulfate dissociate into their components, or are decomposed on dilution with water, this type of solubility test often gives useful hints concerning the presence or absence of certain compounds that form

[3] Conversion into alkali salts can be achieved by a sintering oxidation with a mixture of Na_2CO_3 and $KMnO_4$. Compare F. FEIGL and R. SCHORR, *Z. anal. Chem.* **63**, 10 (1923).

solvates with sulfuric acid, *etc.* The solution colors of iodine and of ferric thiocyanate in organic solvents belong in this category. Brown solutions are obtained if iodine is dissolved in liquids whose molecules contain oxygen or nitrogen, or sulfur atoms that are present in ether-like linkage.[4] In such cases, the iodine is coordinated on these atoms, with formation of brown solvates. Coordination of ferric thiocyanate on oxygen atoms produces solubility, accompanied by the development of a red color.[5] The formation of the characteristic solution colors of iodine and ferric thiocyanate thus provides the possibility of convenient preliminary tests. Other examples of such orienting tests that depend on group actions are: the precipitability of bases with high atomicity from acid solutions as polyiodides or as phosphotungstates; the formation of crystalline picric acid compounds of hydrocarbons, phenols, and amines, by bringing together solutions of the components; the halogen-binding powers (especially addition of bromine) of unsaturated compounds, or rather of carbon double bonds contained in them; the widely used permanganate test for unsaturation. It should also be pointed out that colorless liquid tetranitromethane is an excellent preliminary reagent for ethylene linkages in hydrocarbons, for enolizable compounds, and for unsaturated fatty acids (provided the ethylene linking is not adjacent to the carboxyl group).[6] Intensely colored addition products, soluble in tetranitromethane, are formed with these unsaturated compounds. Consequently, this is another instance of group action.

It is beyond the scope of the present considerations of specificity, selectivity, and sensitivity, to enter into a detailed discussion of preliminary tests in qualitative organic analysis. The cases cited are sufficient to demonstrate that group actions play a significant part here also. Details can be found in works dealing with organic analysis.[7]

DIRECT EXAMINATION FOR CERTAIN ATOMIC GROUPS BY REACTIONS WITH INORGANIC AND ORGANIC REAGENTS

Numerous examples given in Chapter VI showed that a specific or selective action could be attributed to the presence of certain atomic groups in the molecule of the organic reagents used to detect or determine inorganic ions or compounds. Under suitable experimental conditions,

[4] J. PICCARD, *Helv. Chim. Acta* **5**, 243 (1922).

[5] D. DAVIDSON, *Ind. Eng. Chem., Anal. Ed.* **12**, 40 (1940).

[6] J. OSTROMISSLENSKY, *Ber.* **43**, 197 (1910); A. WERNER, *ibid.* **42**, 4324 (1909).

[7] Examples are: O. KAMM, Qualitative Organic Analysis, New York, 1940; P. L. SHRINER and R. C. FUSON, The Systematic Identification of Organic Compounds, 2nd Ed., New York, 1940; F. FEIGL, Qualitative Analysis by Spot Tests, 3rd Ed., New York, 1946; F. SCHNEIDER, Qualitative Organic Microanalysis, New York, 1946; N. D. CHERONIS and J. B. ENTRIKIN, Semimicro Qualitative Organic Analysis, New York, 1947.

minimum quantities of inorganic materials can be detected by organic reagents through the formation of colored or slightly soluble reaction products. Hence the converse effect is fundamentally possible. In other words, it should be feasible to detect certain atomic groups in organic compounds by their direct specific or selective reactions with inorganic reactants. Among the tests based on a direct reaction of certain groups is included also their reaction capability with certain groups in other organic molecules, either by direct salt-formation, condensation, or coordinative addition. A necessary assumption for the analytical employment of a direct reaction is that the change must always occur rapidly with production of characteristic reaction products that are easily seen. For qualitative purposes, complete reaction is not essential, but a prime requirement is that it be possible to detect surely and quickly the occurrence of a reaction involving only minimum quantities of materials.

The following remarks apply to the detection of certain atomic groups in organic compounds because of their behavior with inorganic ions or compounds, and in which they undergo reactions that are the converse of the tests for inorganic materials by means of organic reagents as discussed in Chapter VI. For purposes of inorganic analysis, a specificity of the activity of the organic reagent or of its atomic groups is, of course, more advantageous than a selectivity in its action. The reverse is true for organic analysis, because the selective action of an atomic group toward inorganic compounds signifies that several inorganic reagents are available for the detection of the particular atomic group. The search for new organic reagents to be used in qualitative inorganic analysis will likewise have a bearing on qualitative organic analysis. This applies especially to attempts to ascribe the analytical effects of organic reagents to the action of certain atomic groups. Every extension of knowledge and experience along this line is useful in the development of new test reactions for organic compounds and the groups in them. Several typical examples will be given of the detection of organic atomic groups by tests that are based on their direct reaction with inorganic and organic reactants. All of the reactions cited here have detection limits below 15γ with respect to the materials revealed by them.

1,2-anti-Dioximes R—C—C—R (compare p. 270)
$$\underset{\text{HON} \quad \text{NOH}}{\underset{\|\quad\|}{}}$$
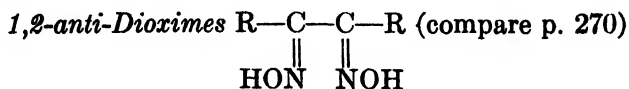
The —C(:NOH)—C(:NOH)— group present in 1,2-*anti*-dioximes exhibits a selective activity toward Ni^{++} and Pd^{++} ions. Water-insoluble, red Ni and yellow Pd salts, which can be considered as inner

complex salts, are formed. It should be remembered that the Ni salts can be precipitated from ammoniacal solutions, and the Pd salts from solutions containing mineral acids.

If 1,2-*anti*-dioximes are tested with respect to their action toward Fe^{++} ions in ammoniacal tartrated solution, it is possible to obtain information about the nature of the radicals bound to the active groups. Aliphatic derivatives form red, water-soluble iron salts, whereas, water-insoluble blue to violet compounds are produced with aromatic dioximes.

$$Acyloinoximes \quad \text{R—CH—C—R (compare p. 266)}$$
$$\quad\quad\quad\quad\quad\quad \underset{\text{OH}}{|} \quad \underset{\text{NOH}}{\|}$$
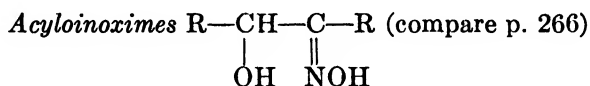
Acyloinoximes are characterized by their action on copper acetate solutions. Green, water-insoluble Cu salts are formed. An insolubility of these copper salts in ammonia indicates that the radicals bound to the active group are either aromatic or are aliphatic residues with long chains.

Another reaction of acyloinoximes with an inorganic reagent is the formation of a precipitate on treatment with acidified solutions of alkali molybdates. This precipitability was discovered by Knowles[8] with benzoinoxime.

Aromatic o-Hydroxyaldoximes $\langle\!\!\!\!\bigcirc\!\!\!\!\rangle$ —C=NOH (compare p. 196)
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \text{OH}$$
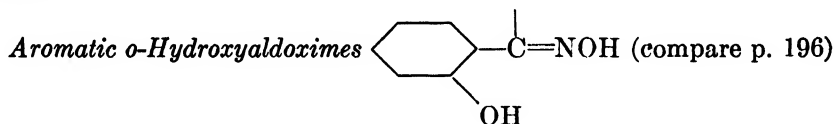
Compounds containing this group are characterized by the formation of yellow-green Cu salts and yellow Pd salts. The action is independent of substituents in the nucleus or on the aliphatic C atom. The Cu salt can be precipitated from acetic acid solutions, the Pd salt from mineral acid solutions. Both are inner complex salts, characterized by being soluble in ammonia.

1,2-Isonitrosoketones R—CO—C(:NOH)—R (compare p. 209)
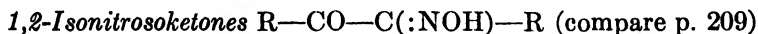
The formation of blue water-soluble ferrous salts is characteristic of compounds containing this grouping, no matter what the radical bound to the C atom, provided it is possible for the CO group to enolize. The ferrous salts form blue solutions in organic solvents; consequently they can be extracted from aqueous solutions.

α,α'-Dipyridyls $\langle\!\!\!\!\bigcirc\!\!\!\!\rangle$—$\langle\!\!\!\!\bigcirc\!\!\!\!\rangle$ (compare p. 319)
$$\quad\quad\quad\quad\quad\quad\text{—N}\quad\quad\text{N—}$$
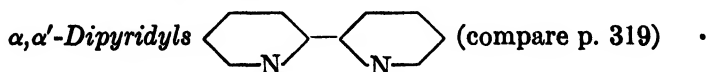
[8] H. KNOWLES, *Bur. Standards J. Research* **9**, 1 (1932).

The characteristic action of this group is its ability to add ferrous ions, with formation of red, acid-stable hexammine ions. Consequently, a mineral acid ferrous salt solution is a suitable reagent. It should be noted that because of size effects the formation of the iron salt is impeded by introducing substituents into the molecule of the α,α'-dipyridyls.

Another reagent for α,α'-dipyridyls may be based on the action observed by Tartarini (see p. 323), who found that highly colored products result from the addition of cuprous halides to the free bases. Possibly, size effects will have a less disturbing influence in this case, but no studies have been made along this line.

Sulfinic Acids R—SO₂H (compare p. 289)

The production of slightly soluble, brown-yellow ferric salts· from mineral acid solutions is characteristic of the sulfinic acid group linked to aliphatic or aromatic radicals. The corresponding sulfinates are also precipitated from acid solutions by uranium^{IV} and cerium^{IV} salts.

Arsonic Acids R—AsO(OH)₂ (compare p. 291)

The precipitating action on zirconium salts exhibited by arsenic acid is retained in the aliphatic and aromatic arsonic acids, which are organic derivatives of arsenic acid. This fact has additional interest because aromatic sulfonic acids (R—SO₃H) have lost the ability so characteristic of sulfuric acid to form slightly soluble barium salts (see p. 429). The zirconium salts of arsonic acids can be precipitated from acid solutions.

Mercaptans and Thioketones R—SH and >C=S (compare p. 145)

It is characteristic of organic compounds containing one of these groups that they catalyze the normally slow reaction:

$$2NaN_3 + I_2 \rightarrow 2NaI + 3N_2$$
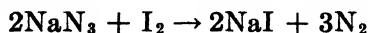
This reaction is initiated in the presence of mercaptans or thioketones (solid or dissolved). Minimal quantities of these compounds can be detected by the resulting evolution of nitrogen. Since other sulfur compounds (thioethers, disulfides, sulfones, sulfonic and sulfinic acids) have no such catalytic action, this iodine-azide test is infallible for mercaptans and thioketones.

Phenols and Polyphenols

All phenols react with aqueous or alcoholic solutions of ferric salts, ferric· chloride being best. Red, violet, or deep green, water-soluble complex ferric phenolates are formed.

Polyphenols, with *ortho*-situated OH groups, react with antimonous

salts, potassium antimonyl tartrate being best. White crystalline precipitates (phenol esters of metantimonous acid) are produced. Polyphenols with three adjacent OH groups react, in mineral acid solution, with antimonous salts and form white crystalline precipitates. Yellow crystalline precipitates are formed, from acid solutions, by bismuth salts. The products are antimonous or bismuth phenolates, respectively (see p. 177).

Nitroso Compounds, Primary Aromatic Amines, and Aliphatic or Aromatic Hydrazines

These materials are characterized by their reaction with the bright yellow water solutions of cyanide salts, such as $Na_2[Fe(CN)_5NH_3]$ or $Na_2[Fe(CN)_5H_2O]$. The complexly bound NH_3 or H_2O molecule is expelled and replaced by a molecule of the nitroso compound, amine, or hydrazine:[9]

$$Na_2[Fe(CN)_5NH_3] + Y \rightarrow Na_2[Fe(CN)_5Y] + NH_3$$
$$Na_2[Fe(CN)_5H_2O] + Y \rightarrow Na_2[Fe(CN)_5Y] + H_2O$$
$$Y = RNO, RNH_2, RNH-NH_2$$
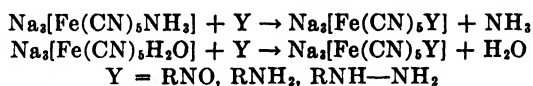
The resulting soluble complex compounds have intense characteristic colors. The photosensitivity of the displacement reaction with nitroso compounds is noteworthy (see p. 689).

Organic Compounds with Reactive CH_2 and NH_2 Groups

1,2-Naphthoquinone-4-sulfonic acid, and likewise its alkali salts, react in basic solution with such organic compounds as contain two mobile hydrogen atoms bound to a carbon or nitrogen atom. Highly colored p-quinoidal condensation products are formed.[10] These reactions can be represented:

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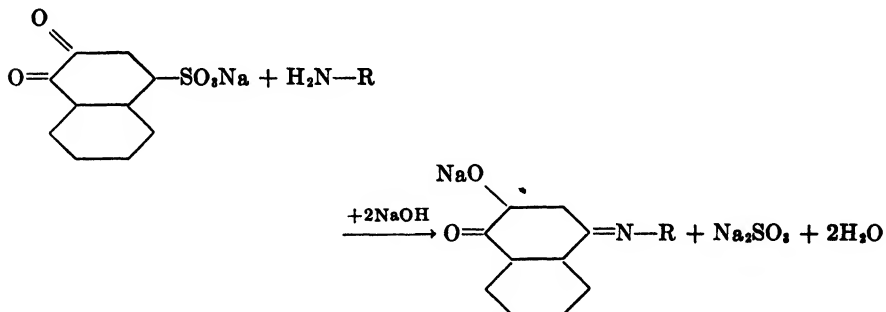
[9] F. FEIGL, V. ANGER and O. FREHDEN, *Mikrochemie* **15**, 181 (1934); V. ANGER, *Mikrochim. Acta* **2**, 3 (1937).

[10] P. EHRLICH and C. A. HERTER, *Z. physiol. Chem.* **41**, 329 (1904).
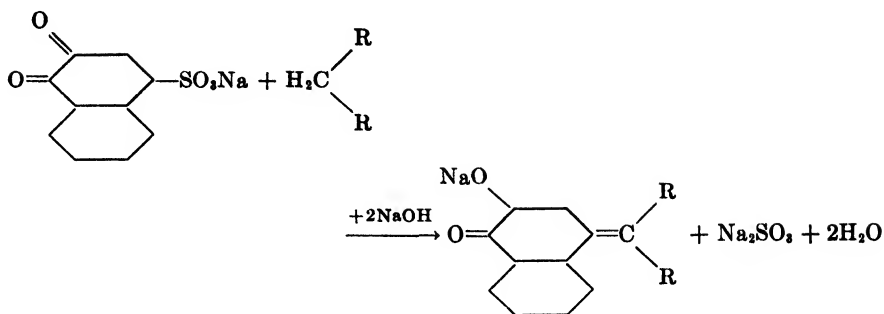
A feature of these reactions, in which the SO₃Na group is replaced by an organic group, is the great reactivity at room temperature.

Conversion of Organic Compounds into Products with Characteristic Atomic Groups

Typical examples were given in the preceding section of reactions of atomic groups in organic compounds with inorganic and organic reagents. The speed of these reactions in aqueous or water-alcohol solutions provided the possibility of selective and, in part, of sensitive tests. In view of the great number and variety of organic compounds, it is easy to see why the number of cases is so limited, in which, from the start, it is possible to count on the presence of atomic groups that can react in this way, in such manner that they may be employed for analytical purposes. Consequently, it is highly important from the standpoint of analytical chemistry that some familiar methods, widely used in making organic preparations, can be utilized for analytical objectives. Such processes include the synthesis, transformation, or degradation of organic compounds. These changes may be utilized in two ways. In the first method, the products obtained by the methods of preparative organic chemistry may have characteristic color, solubility, fluorescence, *etc.* Thus, with a knowledge of the reactions by which they have been formed, it is possible to make deductions as to the identity of the starting materials. In the second case, the methods of preparative chemistry are used to produce compounds containing atomic groups that have characteristic reactions through which they can be identified by suitable tests. These possibilities have several advantages, though it must not be forgotten that sometimes there are unavoidable limitations in applying them. The advantages are that, through preparative operations, the reaction possibilities of the materials to be detected can be utilized. Pertinent examples could be cited to show that, in numerous cases, many years elapsed before analytical chemistry made direct use of these possibilities. A limitation is set by the fact that a reactant essential to preparative

operations often can react with various compounds under the conditions of the experiment. This reduces the unequivocality of such procedures. Furthermore, it should be noted that many preparative operations consume time and material, that incomplete reactions occur, and losses of material are often unavoidable. It is plain that the attainable sensitivities of such tests may be considerably impaired. Nevertheless, "preparative-analytical" methods, some of which possess even microchemical sensitivities, deserve every consideration. Their development and use in spot test analysis will be determined by the extension of micropreparative techniques, a field which is experiencing welcome progress.[11] Several examples of this method of conducting qualitative organic analysis will be given. They are taken from qualitative organic spot tests, in the same way as, in inorganic spot tests, extremely sensitive reactions can be employed exclusively. It must be noted that the activity of certain groups ultimately forms the basis also of the preparative parts of the procedure.

Conversion of Nitro to Nitroso Compounds

Aromatic nitro compounds are easily reduced to nitroso compounds, which are detected readily by the sensitive color reaction with cyanide salts (see p. 377). This reduction can be accomplished by the methods commonly employed in preparative organic chemistry (zinc plus hydrochloric acid, alkali sulfide, etc.). For analytical purposes, the neatest method is to reduce the sample electrolytically, in the presence of a cyanide salt.[12] Nitro compounds can thus be detected even in drops of solution with detection limits of $0.15-3\gamma$.

Conversion of 1,2-Diketones into anti-Dioximes

Aliphatic and monocyclic hydroaromatic o-dioxo compounds (1,2-diketones) react with hydroxylamine to produce 1,2-dioximes. Of these, the anti compound can form red or yellow inner complex nickel salts (see p. 270). This oximation and production of the nickel salt can be accomplished successfully with even minute amounts of test material.[13]

Conversion of Ketomethylene Compounds into anti-Dioximes

Ketomethylene compounds, which contain the group $CO-CH_2$ can likewise be converted into 1,2-dioximes,[13] if the $CO-CH_2$ group is

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[11] See, for example, J. B. and V. NIEDERL, Micromethods of Quantitative Organic Analysis, New York, 1942; F. SCHNEIDER, Qualitative Organic Microanalysis, New York, 1946.

[12] F. FEIGL, V. ANGER and O. FREHDEN, Mikrochemie 15, 183 (1934).

[13] M. ISHIDATE, Mikrochim. Acta 3, 283 (1938).

oxidized to the —CO—CO group.   Selenious acid is excellent for this oxidation.

Conversion of Aromatic Sulfonic Acids into Phenolates

The replacement of an SO_3H group by OH is often accomplished in preparative organic chemistry by fusing with an alkali hydroxide:

$$R—SO_3H + 3NaOH \rightarrow R—ONa + Na_2SO_3 + 2H_2O$$
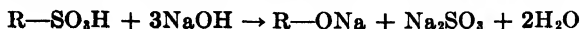
Alkali phenolate and alkali sulfite are formed.   Very sensitive tests for the latter are available.   After carrying out the fusion, which is possible with even minute amounts of test material, a positive response ·to the test for sulfite will prove the presence of a sulfonic acid group bound to an aromatic radical.[14]

Conversion of Primary and Secondary Alcohols into Alkali Xanthates

Primary and secondary alcohols react with carbon disulfide in the presence of alkali hydroxides to produce alkali xanthates:

$$ROH + CS_2 + NaOH \rightarrow CS(OR)(SNa) + H_2O$$
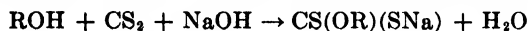
All alkali xanthates react with molybdate, in the presence of mineral acids, to form violet compounds that are soluble in chloroform.   These colored materials are addition compounds of molybdic anhydride and xanthic acid of the general formula $MoO_3·SC(SH)OR$.

The molybdate-xanthate reaction is very sensitive.[15]   Even small quantities of primary or secondary alcohols, after conversion into the corresponding xanthates, can be detected with the aid of acidified molybdate solution.

Conversion of Carboxylic Acids (and Their Derivatives) into Hydroxamic Acids

Carboxylic acids, esters, and anhydrides can be converted readily into hydroxamic acids of the general formula $R·CO·NHOH$.   The procedure is different and characteristic for each class of these compounds.

All hydroxamic acids, in weak acid solution, produce a red or violet color with ferric chloride.   This color reaction is due to the acidic —CO·NHOH group, which is present in all hydroxamic acids.   With ferric iron, inner complex salts are formed, having the structural formula:
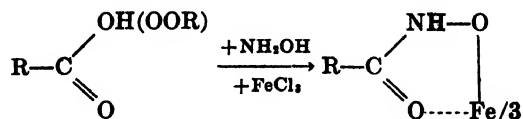
14 F. FEIGL and A. LENZER, *Michrochim. Acta* 1, 129 (1937).
15 D. VITALI, *Boll. chim. pharm.* 38, 377 (1899).

This formation of ferric hydroxamate is used as a test for carboxylic acids and their derivatives.[16]

Free carboxyl groups are converted, by means of thionyl chloride, into acid chlorides which in turn yield alkali hydroxamates when treated with an alkaline solution of hydroxylamine.   Esters react with hydroxylamine and alkali.   Acid anhydrides react directly with hydroxylamine.

Conversion of Amines into Rhodanine Dyes

Compounds containing the NH_2— or NH— groups (including acid amides, pyrrole and its derivatives) give rise to rhodanine dyestuffs (II) on melting with fluorescein chloride (I) and anhydrous zinc chloride.[17] The formation of these dyestuffs is shown in the equation:

$$\text{(I)} + \begin{cases} NH_2R \\ (2NHR_1R_2) \end{cases} \xrightarrow{-2HCl} \text{(II)}$$
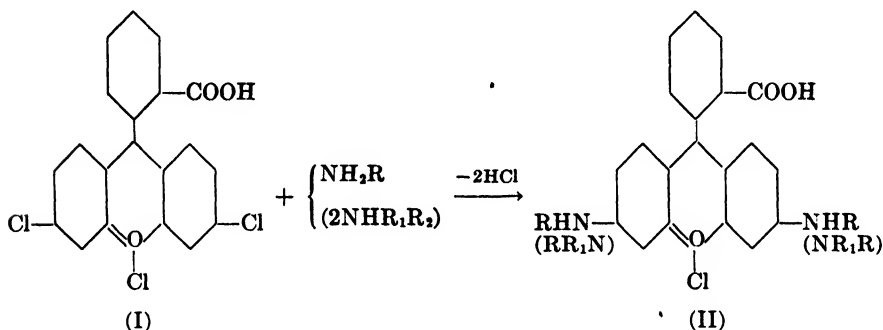
The colors of the resulting dyestuffs differ characteristically in natural and ultraviolet light according to the type of amine involved.   Consequently, not only NH_2— or NH— groups can be detected and differentiated, but it can also be determined whether these groups are linked with aliphatic or aromatic radicals.

[16] F. FEIGL, V. ANGER and O. FREHDEN, *Mikrochemie* 15, 18 (1934).
[17] F. FEIGL, V. ANGER and R. ZAPPERT, *Mikrochemie* 16, 67 (1934).
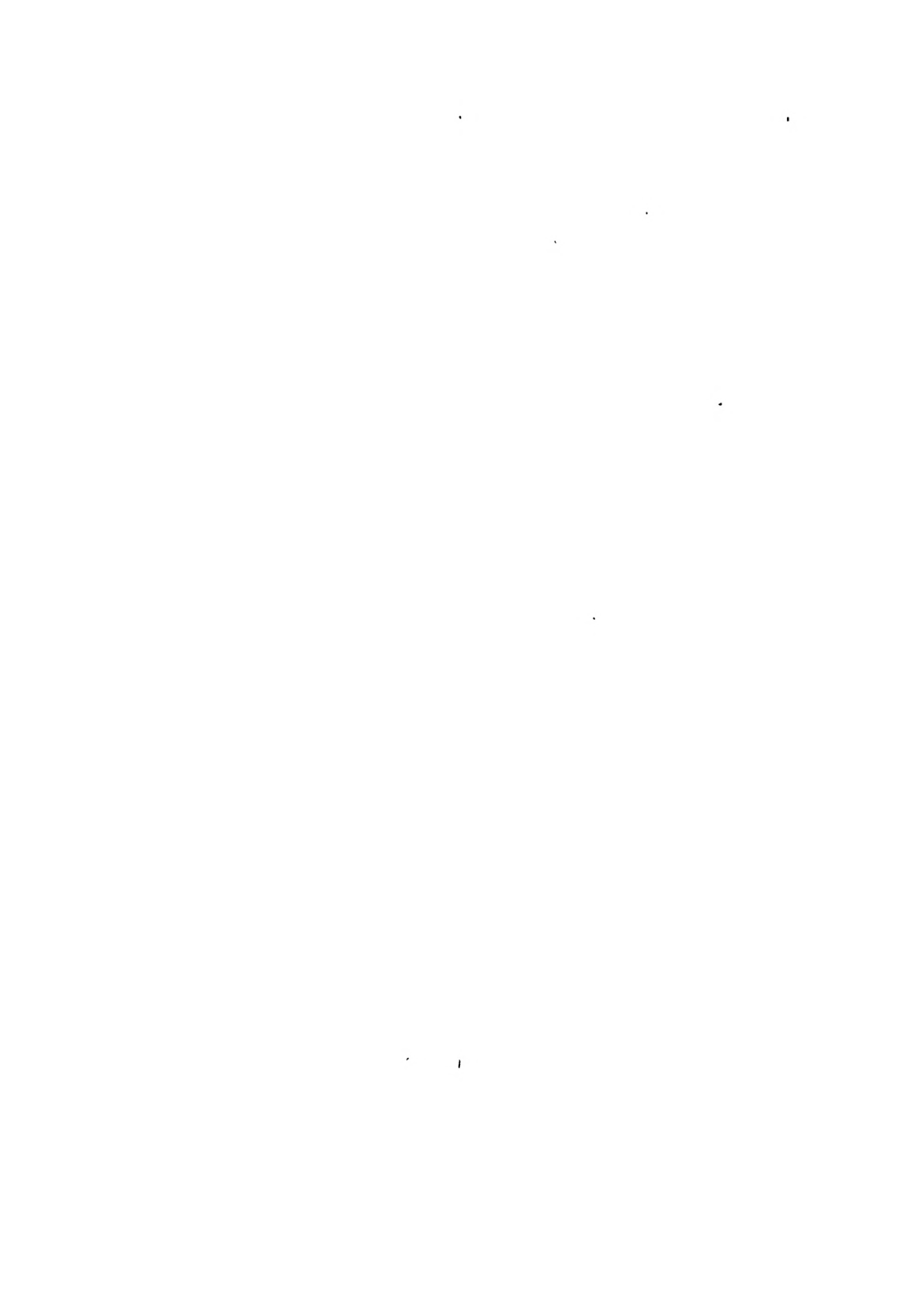
CHAPTER VIII

Regularities and Anomalies in the Solution of Materials in Indifferent Solvents

The preponderant majority of all detection and determination methods used in chemical analysis are based on reactions of dissolved materials. The number of cases in which one reactant is dissolved, and the other is present in an insoluble form, is relatively small. Such instances are encountered almost exclusively in spot test analysis. Reactions of water-insoluble gases with solid or with dissolved reactants, and reactions between two solid reactants, are even fewer in number. Hence, a knowledge of all the factors that play a role in determining the solubility of materials is important.

At present, there are no fixed rules by which it is possible to predict whether a particular substance will dissolve in a given inert solvent and, if it does, to what extent. Hence, actual trial is the only method of ascertaining these facts. Nevertheless, there are certain theoretical considerations and experimentally derived rules that are sometimes useful in making predictions concerning solubility. These regularities, which rest primarily on relations between solubility and constitutional factors in the structure of the solute and the solvent, will be discussed in this and the following chapter.

The definition of a true solution includes the disappearance of phase differences. The prerequisite for this condition is the possibility of complete penetration and miscibility of two materials. The material present in greater quantity is generally termed the solvent, the other is called the solute. A parallel can be drawn between the dissolving of a solid material in a liquid solvent and the vaporization of a solid: the lattice forces holding together the smallest structural units of the solid have to be overcome. In normal vaporization, which is an endothermic process, the requisite energy must be supplied in the form of heat. Consequently, energy must always be applied also to overcome the lattice forces during the process of solution. The chief source of this energy is the reaction between the units of the lattice—molecules or ions—and molecules of the solvent. This energy-furnishing process is known as "solvation," the special case of solution in water being termed "hydration." The products are called "solvates" and "hydrates," respectively. The solvation not only furnishes the energy necessary to overcome the lattice forces, but at the same time it gives rise to products that are more like the molecules of the solvent.

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If the result of solvation is to produce a similarity between the molecules of the solvent and those of the solvate, it is logical to expect excellent solubility in such cases as those in which, from the beginning, there exists a similarity between the molecules of the solvent and those of the material that is to be dissolved. Many confirmations of this statement are provided by organic compounds, among which it is easy to find such similarities if suitable choices are made on the basis of constitution or structure. Thus, liquid and solid hydrocarbons are not soluble in water, but they dissolve well in benzene and other hydrocarbons, to which they are closely related chemically. The reverse behavior, namely, excellent solubility in water and insolubility in hydrocarbons, is exhibited by polyhydric alcohols (sugar, for instance) which, because of their content of OH groups, can be regarded as organic derivatives of water. Frequently, hydrocarbons are soluble in primary alcohols. In such cases, it has been found that the lower alcohols, which have fewer carbon atoms, show a proportionately lower solvent power than the higher alcohols. The latter are also better solvents than the lower alcohols for palmitic acid, $CH_3(CH_2)_{14}COOH$, which has a high carbon content. In this connection, it is interesting to note that the ability of esters of acetic acid to dissolve palmitic acid increases with an increasing number of carbon atoms in the radical bound to the CH_3COO group. The facts that the aromatic hydrocarbons naphthalene and anthracene dissolve in aliphatic hexane (C_6H_{12}) only to the extent of 14% and 9%, respectively, while the corresponding figures in aromatic benzene (C_6H_6) are 36% and 49%, and that picric acid is distinctly more soluble in aromatic than in aliphatic hydrocarbons,[1] are in agreement with the examples just given. Such findings all emphasize the fact that similarity of certain atomic groups in the molecules of solvent and solute is significant in determining solubility. This rule, which has general application,[2] is plainly evidenced in the behavior of dipicrylamine, $NH[C_6H_2(NO_2)_3]_2$, and of its thallium and potassium salts, which are difficultly soluble in water. At room temperature, dipicrylamine is only slightly soluble in benzene, and the salts do not dissolve at all. On the other hand, dipicrylamine, and also its salts, dissolve readily in nitrobenzene, in fused polynitrobenzenes, and in nitronaphthalene.[3] The decisive importance of the presence of NO_2 groups in determining this solubility in nitro compounds, in other words, that this is a typical group action, is shown by the fact that dipicrylamine and its salts are easily

[1] I. TAUSZ and E. SCHNABEL, *Chem. Ztg.* **43**, 726 (1919).

[2] See O. KAMM, Organic Analysis, 2nd Ed., New York, 1940, concerning solubility regularities among organic compounds.

[3] F. FEIGL, L, I. MIRANDA and H. A. SPINELLI, *Bol. Lab. Prod. Min.* **11**, 81 (1943).

soluble even in nitromethane, whose structure is the simplest of the organic nitro compounds. The experiments of Walden[4] on the solubility of tetraalkylammonium iodides in certain organic solvents are of interest in this connection. In the series NR_4I ($R = CH_3$, C_2H_5, C_3H_7, C_6H_{11}), the solubility in alcohols, aldehydes, and ketones, often increases by several powers of ten, with rising carbon content of R. Thus 100 ml. of ethyl alcohol dissolve only 0.048 g. of $N(CH_3)_4I$, in contrast to 20 g. of $N(C_3H_7)_4I$. Hence, the accumulation of carbon-rich radicals, distinctly enhances the solubility of this type of salt in organic solvents.

The effect of similarity in constitution is shown strikingly by the behavior of inner complex salts toward melts of their respective complex formers. Feigl and coworkers[3] showed that all inner complex salts seem to be soluble in melts of their particular complex former. Colored inner complex salts often produce more intensely colored melts of this type, from which, on cooling, the original inner complex salt separates unaltered. The ready solubility of inner complex salts in melts of the complex former becomes understandable if the constitution of inner complex salts is compared with that of the complex former. An inspection of the structural formula of 8-hydroxyquinoline, as contrasted with that of one of its inner complex salts, e.g., aluminum oxinate

shows the greatest conceivable similarity in constitution. The same is equally apparent if the structural formulas of other complex salts and their complex formers are placed side by side. Obviously, this is why complex salts in general dissolve in melts of their respective complex formers.[4a]

The foregoing examples show an indubitable kinship between solubility and similarity in constitution of solvents and solute. Hence, analogously constituted compounds, for the most part, behave in the same manner toward a given solvent which resembles them in constitution because it contains similar atomic groups. The relations in behavior of analogously constituted compounds toward solvents with which they have no constitutional similarity are far less clear and uniform. In such

[4] P. WALDEN, Elektrochemie nichtwässeriger Lösungen, p. 455 ff. Brunswick, 1926.

[4a] F. FEIGL and L. BAUMFELD, Anal. Chim. Acta **2**, 430 (1948), described an interesting application of the formation and solubility of ferric and vanadium oxinates in fused 8-hydroxyquinoline for the detection of iron and vanadium.

cases, analogously constructed compounds can exhibit striking differences in their solubility characteristics. An instructive instance of similar and dissimilar behavior of analogously constituted compounds toward solvents of similar and dissimilar constitution is provided by caffeine (1,3,7-trimethylxanthine) and theobromine (3,7-dimethylxanthine). Both are quite soluble in aniline and methylaniline. The effect of similarity is evident here, since the molecules of the solvents and the solutes contain basic nitrogen atoms. In contrast, caffeine is readily soluble in hot kerosene, while theobromine is insoluble.[5] This fact is striking because these alkaloids have practically the same constitution throughout, and differ only by the extra CH_3 group in caffeine.

Many facts justify the conviction that the dissolution of a material never occurs without simultaneous solvation. Accordingly, every process of dissolution of liquids and solids should be regarded as a chemical reaction leading to the formation of solvates. In this sense, all solvents are chemically active. As to the composition of solvates in solution, exact statements can be made only in individual cases. For instance, the composition of ion hydrates has been established by physicochemical measurements. Many cases involve compounds which correspond to coordination compounds that had been isolated as solids. In contrast, the association of the components is quite loose in other instances, and the union is maintained only in solution. In any event, there can be no essential differences in the forces that are responsible for the ligation in either stable or loose addition compounds. Solutions may quite generally be regarded as equilibrium systems between molecular compounds of the most divergent kinds, whose particular nature and composition may differ from case to case. The chemical character of solution processes is evidenced by the heat effects observed in many instances, by the volume contraction when liquids are mixed, by the anomalous vapor pressure and viscosity of mixtures of liquids, by the color changes that accompany solution processes, and by the fact that materials deposited from solution on crystallization or precipitation often retain molecules of the solvent in their crystal lattices. Particularly obvious illustrations of this latter result are provided by compounds that contain "water (alcohol, ether, benzene) of crystallization" and the like, as well as by the numerous so-called molecular compounds of purely organic or mixed inorganic-organic nature, that are produced in solution by addition reactions.

In view of the analytical importance of the solution process and of solubility characteristics, it must be remembered that there are no

[5] F. FEIGL, unpublished studies. These findings served as the basis for a new technical process for extracting caffeine, widely used in Brazil during the last war.

general infallible relations between the fixation of solvent molecules on a compound and its solubility. In the case of water acting as solvent (the same is true of organic solvents), it is found that many compounds that are quite soluble ($NaCl$, KCl, $HgCl_2$, *etc.*) come out of solution with no water of crystallization, while, on the other hand, many even slightly soluble compounds separate with water of crystallization. Instances of the latter type include the purely inorganic compounds, $MgNH_4PO_4\cdot6H_2O$; $ThF_4\cdot4H_2O$; $BeCO_3\cdot4H_2O$; $(NH_4)_3PO_4\cdot12MoO_3\cdot6H_2O$; $K_3Co(NO_2)_6\cdot3H_2O$. Similar cases among salts of organic acids and inner complex salts are: $NaZn(UO_2)_3(C_2H_3O_2)_9\cdot6H_2O$; the oxalates of calcium and thorium with 2 and 6 molecules of water of crystallization, respectively; the hydroxy-quinolates of magnesium, manganese, cobalt, nickel, cadmium, and zinc, each with 2 molecules (these hydrates are just as slightly soluble as other water-free metal oxinates); cobaltic α-nitroso-β-naphthol with 2 molecules; calcium picrolonate with 8 molecules, whose precipitation sensitivity is twice as great as that of lead picrolonate, which contains only 1.5 molecules of water of crystallization. All these compounds, despite their content of chemically bound water, are so slightly soluble that their precipitation from aqueous solutions is the basis of quantitative methods of determination. Salts of organic bases, particularly alkaloids, as well as metal salts of organic acids, provide instances which show that there is no necessarily direct connection between water of crystallization and solubility in water. Thus the chloride and sulfate of emetine both crystallize with 7 molecules of water. Nevertheless, 100 ml. of saturated solution of the chloride contains only 13 g. of the salt, in comparison with the more than 100 g. present in a like volume of the saturated solution of the sulfate.[6] Codeine sulfate with 5 molecules of water of crystallization is much less soluble than the phosphate which carries only 2 molecules (3.3 g. against 44.9 g. in 100 ml. water).[7]

All experience with purely organic compounds shows that the ability to fix water molecules is shown only by distinctly acidic or basic compounds. This indicates a localization of the H_2O-addition on the acidic or basic groups of the molecule. Organic compounds containing water of crystallization conform to the rule: if they are not soluble in cold water they will become so when the temperature of the solvent is raised. This is in fundamental contrast to the behavior of inorganic compounds, among which, as already stated, even hydrated salts may remain insoluble in hot water. Some anhydrous organic compounds are quite soluble in water. Typical instances are certain aromatic carboxylic and

[6] F. H. CARR and F. L. PYMAN, *J. Chem. Soc.* **105**, 1602 (1914).

[7] E. BARONI and O. BARLINETTI, *J. Pharm. Phys.* **60**, 193 (1911); *Chem. Abstracts* **6**, 272 (1911).

sulfonic acids. It should also be emphasized in this connection that at 25°C. anhydrous 1,2,3-trihydroxybenzene (pyrogallol) is soluble to the extent of 62% in water, while the isomeric 1,3,5-trihydroxybenzene (phloroglucinol), despite the presence of 2 molecules of water of crystallization, is only 1% soluble.[8] This difference shows that constitutional factors are also important in determining the solubility of organic compounds in water. The foregoing examples of the behavior of inorganic and organic compounds toward water demonstrate that it is not permissible to draw conclusions as to the degree of hydration in the solution, or regarding the solubility itself, from the mere fact that a solid compound contains water of crystallization.[9] However, it must always be kept in mind that hydrates are present in water solutions: hydrated molecules in the cases of non-electrolytes, and hydrated ions in solutions of electrolytes. This is the basis of the long known and widely used process of salting-out slightly soluble organic compounds from their aqueous solutions by adding considerable quantities of quite water-soluble neutral salts. As these salts dissolve, and requisition water molecules to form hydrates, the solvent is withdrawn from the previously dissolved and hydrated compounds; the result is supersaturation followed by precipitation.

Although, as noted, no conclusions may be reached from the water content of a solid compound as to its definite degree of hydration in solution nor regarding its solubility, nevertheless, it is significant that anhydrous and hydrated compounds of the same kind are often distinguished by considerably different rates of solution. For example, crystal soda ($Na_2CO_3 \cdot 10H_2O$) dissolves more rapidly in water than anhydrous soda. Anhydrous $CrCl_3$ is practically insoluble in water, in contrast to the quite soluble $CrCl_3 \cdot 6H_2O$. Anhydrous $PdCl_2$ is only slightly soluble, whereas $PdCl_2 \cdot 2H_2O$ is hygroscopic and quite water-soluble. $MgSO_4 \cdot 5H_2O$ dissolves far more rapidly than anhydrous $MgSO_4$, and the same is true of gypsum ($CaSO_4 \cdot 2H_2O$) as contrasted with anhydrite ($CaSO_4$). A reaction for distinguishing the two varieties of calcium sulfate is based on this fact.[10] Hydrated and water-free sulfates of cobalt, and particularly those of nickel, show very distinct solubility differences,[11] or more correctly, differences in the rate of solu-

[8] W. M. DEHN, J. Am. Chem. Soc. **39**, 1400 (1917).

[9] Compare R. SCHOLDER, Ber. **60**, 1523 (1927).

[10] F. FEIGL, Spot Tests, p. 447.

[11] If a $CoSO_4$-$NiSO_4$ solution is evaporated and the residue heated, the mixture of the anhydrous sulfates dissolves in water far more readily than anhydrous nickel sulfate alone. Obviously, the dissolving of the $CoSO_4$ induces the solution of the $NiSO_4$. A similar effect is observed with a mixture of anhydrous $MgSO_4$ and $NiSO_4$ (unpublished studies by F. FEIGL).

tion. The observation of Weinland and Ensgraber[12] is pertinent. They found that the compounds $[Fe(SO_4)_2]R$ ($R = NH_4$, $K + H_2O$, $H \cdot C_5H_5N + 2H_2O$) which differ from the familiar and easily soluble alums merely through the deficiency of water of crystallization, are, in contrast to these, almost insoluble in water. Only after long shaking, during which a slow hydration obviously occurs, can a solution be obtained that is identical with that of iron alums $[Fe(SO_4)_2]R \cdot 12H_2O$.

The fact that compounds which carry water of crystallization have a higher rate of solution than the corresponding anhydrous compounds is a strong argument for the concept that solvate-water molecules join to water molecules that are already bound or coordinated. Evidence favoring this idea is provided by the interesting findings of Ephraim[13] with regard to the water-solubility of cobalt ammines. Comparison of the hexamminocobaltic salts (luteo salts) with the corresponding mono-aquopentamminocobaltic salts (roseo salts) shows that the latter are much more soluble. The reason doubtless is that the complex cation $[Co(NH_3)_5H_2O]^{+++}$ of the roseo salts contains one molecule of water in contrast to the cation $[Co(NH_3)_6]^{+++}$ of the luteo salts. The replacement of a second molecule of ammonia of the luteo salts to produce the dia-quotetramminocobaltic salts, with the cation $[Co(NH_3)_4(H_2O)_2]^{+++}$ results in a further increase in solubility. These solubility relationships are shown in Table XI.

TABLE XI

Solubility of Cobalt Ammines

(G.-mols./l. of water)

Anion	$[Co(NH_3)_6]^{+++}$	$[Co(NH_3)_5H_2O]^{+++}$	$[Co(NH_3)_4(H_2O)_2]^{+++}$
Chloride..............	0.20	0.86	1.83
Bromide..............	0.040	0.346	1.67
Nitrate...............	0.033	0.153	1.03
Sulfate..............	0.015	0.047	0.175
Perchlorate..........	0.013	0.207	
Iodide...............	0.015	0.155	
Oxalate......... ...	0 0007	0.0019	
Dichromate....... ..	0.00029	0.00037	

These data are very informative because none of these cobalt ammines carries water of crystallization, they are stable in water solution, and the various salts taken for comparison have practically identical molecular weights. Consequently, the water-solubility of these compounds does not involve differences in solution rates as in the preceding examples, but

[12] R. Weinland and F. Ensgraber, *Z. anorg. allgem. Chem.* **84**, 340 (1913).

[13] F. Ephraim, *Ber.* **56**, 1530 (1923).

differences in the actual extents of solubility. The increments due to such step-wise replacement of ammonia molecules by water molecules can be considerable. This is best illustrated by the three bromides. Their respective solubilities (g./100 ml. water) are: luteo salt, 1.6; roseo salt 13.9; diaquo salt 67.1. A further inspection of the table shows that these solubility differences are not limited to the fairly soluble cobalt ammines; the difficulty soluble oxalates and dichromates show the same progression. Along this line, it is interesting to note the solubility of the cobalt ammines of naphthalene-β-sulfonic acid. The figures for the luteo, roseo, and diaquo salts are: 0.0005, 0.0006, and 0.0027 g.-mols./l. These sulfonates crystallize with 3 or 6 molecules of water. Hence, the water of the water of crystallization does not promote solubility in these instances, or, rather, the effect is much less than the effect of the water molecules which are complexly held in the cation.

Clear examples of the chemical nature of solution processes are encountered in the behavior of inorganic and organic compounds toward binary mixtures of solvents. If the dissolution of a material and the mixing of solvents were purely physical processes, the extent of the solubility of a material in a binary mixture of solvents would be an additive function of the individual solubilities. However, numerous cases of wide deviations from such additivity can be found. The studies of Dehn and of Pucher and Dehn[14] on the solubility of many organic com-

TABLE XII

Solubility (in g.) in 100 g. Water, Pyridine, and Water-Pyridine (1 : 1)

Solute	Water	Pyridine	Water-pyridine	Δ of additivity
Acetamide..	97.50	17.75	84 70	+27.1
Acetanilide..............	0.55	48.61	55.50	+30.9
Azobenzene..............	0.03	76.44	16 78	−21.5
Azolitmin...............	39.50	0.05	0.12	−19.66
Benzamide..............	1.35	31.23	39 15	+22.9
Benzoin.................	0.03	20.20	6.63	− 3.5
Brucine.................	0.05	28.00	46 11	+32.08
Cholesterol.............	0.26	68.10	1.10	−33.08
m-Dinitrobenzene........	0.05	106.30	45.50	− 7.68
Fluorescein..............	0.005	13.29	37.22	+30.57
Glycine.................	51.00	0.61	0 74	−25.06
Helianthine.............	0.02	0.75	62.50	+62.12
Iodoform	0.01	173.10	22.39	−64.1
Methyl orange...........	0.02	1.80	51.50	+50.6
Methyl oxalate...........	6.18	4.80	93.10	+87.61
Thiourea................	9.10	12.50	41.20	+30.4

[14] W. M. DEHN, *J. Am. Chem, Soc.* **39**, 1378, 1400 (1917); G. PUCHER and W. M. DEHN, *ibid.*, **43**, 1753 (1921).

pounds in mixtures of solvents will be given first. Some of these data, which are characteristic, are contained in Table XII. (The solubilities were determined at room temperature.)

These data show that the solubility of organic compounds of the most varied types, is sometimes greater, and sometimes less in a water-pyridine mixture than corresponds to an additivity of the solubilities. In this respect, the behavior of organic compounds toward alcohol-quinoline mixtures is quite interesting (see Table XIII).

TABLE XIII

Solubility (in g.) in 100 g. Alcohol, Quinoline, and Alcohol-Quinoline (Equimolar)

Solute	Alcohol	Quinoline	Alcohol-quinoline	Δ of additivity
Acetamide..............	21 30	1.67	23.69	+ 8 74
Benzamide.......... .	17.30	6.27	18.55	+ 9 37
Benzidine.............	7.68	43.07	47.23	+ 13 44
Carbazole.......... ..	1 30	33.40	9.86	− 15 10
Chloral hydrate....... ..	215.0	12.56	0.58	− 65.22
Cinnamic acid........:..	22 03	1 85	132.40	+125.25
Ethyl urea.............	79 95	1.13	5.55	− 16.31
Hippuric acid..........	4.60	20.10	47.23	+ 31.19
Indole.................	35.85	11 30	12.00	− 5.82
o-Nitrophenol.	404.0	1450.0	1000.0 .	−176 0
Quinine.....	166.60	22 28	30.04	− 30.23
Vanillin.......	67 22	5.51	64.30	+ 42.55

The solubility anomalies shown in the foregoing tables can be explained plausibly on the basis of the chemical nature of the solution process, if the following possibilities are taken into account: (a) The two solvents form addition compounds (solvates) with each other. The solute then is not confronted by a mixture, but by an essentially new solvent. This condition undoubtedly is met in $H_2O—C_5H_5N$ mixtures, since hydrates of pyridine are known. (b) The formation of an addition compound, as in (a), lowers the concentration of the better solvent partner of the mixture. (c) The solute unites with molecules of one of the solvents to form an addition compound, and thus produces a new compound with a different solubility. The behavior of acid compounds toward the bases pyridine and quinoline illustrate this possibility. (d) The solute combines with the solvates formed from the solvent and produces addition compounds whose solubility relationships are quite different from those of the pure solute. If it is further considered that the processes listed under (a) to (d) can occur concurrently and may overlap, deviations from an additivity in the solubility can be expected in all instances, and to varying degrees. The findings of Dehn and Pucher provide experimental proofs of this.

There are many examples of solution anomalies of inorganic materials in alcohol-water mixtures, and some instances in mixtures of organic solvents.[15] Bruner[16] found that the solubility of iodine in mixtures of chloroform with ethyl alcohol, carbon tetrachloride, carbon disulfide, and benzene, is less than corresponds to the quantities of the solvents. On the other hand, the solubility of iodine in mixtures of carbon disulfide with benzene or toluene is greater than the calculated amount,[17] whereas, in mixtures of benzene with toluene, the solubility of iodine equals the sum of the individual solubilities. Timofejev[18] found that mixtures of one part of methyl alcohol with one or two parts of benzene dissolve considerably less mercuric chloride than the quantity calculated from its solubility in the separate solvents. Interesting anomalies were observed by Wright.[19] He noted that the solubility in 50% alcohol of NaCl, KCl, KBr, and KNO$_3$ was raised considerably by the addition of benzene, carbon tetrachloride, or ethyl acetate. For instance, the solubility of sodium chloride was increased from 6.4 g. to 13.4 g. when 100 grams of 1:1 water-alcohol mixture was shaken with carbon tetrachloride. The explanation is that the water-alcohol mixture contains solvates, and the alcohol is withdrawn from them by the carbon tetrachloride. Consequently, more free water molecules are made available for dissolving the sodium chloride with formation of hydrates of sodium chloride or its hydrated ions. Conversely, carbon tetrachloride dissolves far better in a water-alcohol mixture when sodium chloride is present. In this case, the sodium chloride removes water from the alcohol-water solvates, and thus raises the concentration of free alcohol available for dissolving carbon tetrachloride.

This discussion of anomalies in the solubilities of inorganic materials in mixtures of organic solvents should be supplemented by a short comment on the analytically important fact that anhydrous salts and likewise those carrying water of crystallization (and accordingly also water solutions of salts) often exhibit marked differences in behavior toward organic solvents. Thus, the vitriols, MeSO$_4 \cdot$7H$_2$O (Me = Cu, Co, Ni, Zn, Mg), are far more soluble in absolute methyl alcohol than the corresponding anhydrous sulfates.[20] This influence of the water content is also illustrated by the fact that the solubilities of NiSO$_4 \cdot$7H$_2$O, NiSO$_4 \cdot$6H$_2$O, and NiSO$_4$ in 100 ml. of methyl alcohol are 48 g., 31.6 g., and 0.5

[15] A comprehensive survey of the literature is given by P. WALDEN, *op. cit.* (p. 385), p. 474.

[16] L. BRUNER, *Z. phys. Chem.* **26**, 145 (1898).

[17] H. N. DAWSON, *J. Chem. Soc.* **81**, 1086 (1902).

[18] Cited by P. WALDEN, *op. cit.* p. 475.

[19] R. WRIGHT, *J. Chem. Soc.* **129**, 1203 (1926).

[20] Taken from P. WALDEN, *op. cit.* p. 444 ff.

g., respectively. Likewise, $NiCl_2 \cdot 6H_2O$ and $CH_3COONa \cdot 3H_2O$ are more soluble in ethyl alcohol than the anhydrous salts. On the other hand, the solubility (8.3 g.) of $NaI \cdot 2H_2O$ in ethyl alcohol is less than that (43.1 g.) of anhydrous NaI. Willard and Smith[21] have furnished clear examples of solubility differences between hydrated and anhydrous salts. They found that $LiClO_4 \cdot 3H_2O$ is less soluble than anhydrous $LiClO_4$ in all the alcohols tested, as well as in acetone, and ethyl acetate. Anhydrous $LiClO_4$ forms a viscous solution in ether containing up to 52% of the salt, while $LiClO_4 \cdot 3H_2O$ dissolves only to the extent of 0.2%. These examples show that hydrated and anhydrous salts can behave as two entirely different compounds with respect to solubility in a given organic solvent.

Modifications of the solubility of a compound in an organic solvent by the addition of a second solvent, as well as the divergent solubilities of hydrated and anhydrous salts, not only serve to illustrate the chemical character of solution processes, but in addition such solubility differences may have practical significance in analytical chemistry. Organic solvents are often used for preparing reagent solutions, for separating the ingredients of a mixture of solids,[22] and for extracting reaction products or the components of a solution.[23] In such cases, solution anomalies may produce desirable or undesirable effects, that cannot be foreseen but which can be determined empirically.

The following observation, by Yoe and Hall[24] is an example of a

[21] H. H. WILLARD and G. F. SMITH, *J. Am. Chem. Soc.* **45**, 286 (1923).

[22] In quantitative inorganic analysis, the most important and, in part, the only reliable methods for separating alkali metals are based on differences in the solubility of the chlorides and perchlorates in organic solvents and mixtures of such solvents. The solubility of LiCl in amyl alcohol makes it possible to separate lithium chloride from the other alkali chlorides [F. A. GOOCH, *J. Am. Chem. Soc.* **9**, 33 (1887)]. The solubility of $NaClO_4$ and $LiClO_4$ in a mixture of *n*-butyl alcohol and ethyl acetate, and the precipitation of· NaCl from this solution by passing in HCl, serves to separate $NaClO_4$ and $LiClO_4$ from other alkali perchlorates, and also to separate sodium from lithium. Compare H. H. WILLARD and G. F. SMITH, *J. Am. Chem. Soc.* **44**, 2816 (1922); G. F. SMITH, *ibid.* **47**, 762, 774 (1925). Not only $LiClO_4$, but all lithium halides, are strikingly soluble in organic solvents containing oxygen atoms. This indicates the formation of solvates of the lithium salts by coordination on the oxygen atoms of the solvent. Molecular compounds of lithium halides with monohydric alcohols have actually been isolated [W. TURNER and C. BISSET, *J. Chem. Soc.* **105**, 1777 (1914)]. According to J. ZWIKKER [*Pharm. Weekbl.* **54**, 101 (1917)], cholesterol in oils can be detected through the slight solubility in pyridine of the molecular compound $C_{27}H_{45}OH \cdot LiCl$.

[23] Another type of the analytical employment of organic solvents which are not miscible with water depends on the accumulation of slight, scarcely visible precipitates in the water-organic liquid interface. This "analytical flotation" is discussed in Chapter X.

[24] J. H. YOE and R. T. HALL, *J. Am. Chem. Soc.* **59**, 872 (1937).

desirable anomaly in the solubility of organic reagents. Ferron (see p. 187), the most sensitive organic reagent for iron, exhibits the following solubilities:

Solvent	*G. ferron-100 ml. solvent*
Water......................	0.2220
Alcohol (absolute)...........	0.0304
Acetone...................	0.0080
Water-alcohol (1:1).........	0.3500 instead of 0.1267 (Δ = +0.2233)
Water-acetone (1:1)........	0.7200 instead of 0.1150 (Δ = +0.6050)

In every case, the difference between the lattice energy and the solvation energy is primarily the decisive factor in determining the solubility of solid materials. Doubtless, constitutional influences also play a role, because it can be expected that the extent of the solvation, and therefore the solvation energy, will be increased with compounds that are made capable of solvation by certain atoms or groups. Consequently, relationships between the possibility of binding water and solubility often exist in the case of organic compounds. For instance, $C_6H_5SO_3H \cdot H_2O$, $C_6H_3(SO_3H)_3 \cdot 3H_2O$, and $C_{10}H_7SO_3H(\beta) \cdot H_2O$ are all soluble in water. Thus there is no doubt that in these sulfonic acids the SO_3H group has the ability to bind water. Since the number of water molecules equals the number of SO_3H groups, it is almost certain that the acidic H atom is the coordination center for the formation of hydrates. This does not mean, however, that all aromatic sulfonic acids in the solid state always bind one molecule of water on each SO_3H group. There are water-free sulfonic acids, and also some that contain more water than this 1:1 ratio. For instance, p-toluenesulfonic acid carries $4H_2O$ and o-toluenesulfonic acid has $2H_2O$. In this connection it may also be noted, that anhydrous β-naphthalenesulfonic acid is easily soluble in cold benzene or toluene, while only 1 part of the hydrated acid is taken up by 500 parts of boiling benzene.[25]

The existence of hydrates in aqueous solution is also supported by a number of physical facts.[26] Accordingly, there is no doubt that the ability to add water is an important factor in the solubility of materials in this solvent. As this addition is a result of the action of combining forces, it must be localized on certain atoms or groups of a molecule. Such groups act, to an extent, as promoters of the solubility and so acquire a functional importance in organic reagents and their reaction products. Several examples will be given.

[25] The solubility data cited in this and the following chapter are taken from F. BEILSTEIN, Handbuch der organischen Chemie, 4 ed. Berlin, 1918, and A. SEIDELL, Solubility of Organic Compounds, New York, 1941.

[26] Compare the extensive compilation of R. FRICKE, Z. Elektrochem. **28**, 161 (1922).

The activity of the SO_3H group in promoting solubility is exhibited in the water-solubility of benzenesulfonic acid and naphthalenesulfonic acid. Analogous solubilizing effects are encountered in the mono-phenylated phosphoric, arsenic, and boric acids: Hot water dissolves $C_6H_5(PO)(OH)_2$, $C_6H_5(AsO)(OH)_2$, and $C_6H_5B(OH)_2$. In contrast, the corresponding diphenylated acids are not soluble in water, but are quite soluble in organic liquids. The hydration ability of the single OH groups, which are not bound to the organic portion of the diphenylated acids, obviously is not sufficient to carry the entire molecule into solution in water. Acidic groups, in general, are capable of promoting the solution of organic compounds in water. This effect is evident not only in the foregoing examples but also in the activity of the COOH group. For instance, benzoic acid is rather soluble in hot water. It can be regarded as phenylcarbonic acid and hence, corresponding to the relatively weak acidic character of the slightly soluble carbonic acid, the solubility promoting action of the COOH group is less than that of the SO_3H group. Table XIV shows the effect of introducing the COOH group into the C_6H_6 molecule, and the enhancement of the carboxyl effect by supplementary introduction of phenolic OH groups. These data also show that, with isomeric compounds, an additional effect is exerted by the position of the solubilizing groups. There is a general rule that the solubility of isomers decreases as the melting point rises. Hence, the melting point is included in Table XIV.

TABLE XIV

Compound	.Formula	Solubility at 25°C. g./100 ml.
Benzene................	C_6H_6	0.171
Benzoic acid..........:........ ...	C_6H_5COOH	0.29 (120°C.)
o-Hydroxybenzoic acid	$C_6H_4(OH)COOH$	1.80 (158°C.)
m-Hydroxybenzoic acid.............	$C_6H_4(OH)COOH$	0.85 (200°C.)
p-Hydroxybenzoic acid.............	$C_6H_4(OH)COOH$	0.50 (213°C.)
o-Benzenedicarboxylic acid.........	$C_6H_4(COOH)_2$	0.70 (230°C.)
m-Benzenedicarboxylic acid	$C_6H_4(COOH)_2$	0.013 (300°C.)
p-Benzenedicarboxylic acid..........	$C_6H_4(COOH)_2$	Insoluble (sublimes)

Table XV shows that the introduction of OH groups into the benzene or toluene molecule sometimes tends to promote solubility. The position of the OH groups with respect to each other is of great importance, whereas the position of the CH_3 group in the cresols has no marked influence. The relatively slight solubility of hydroquinone appears striking among the three dihydroxybenzenes. The reason possibly being

that it is not present exclusively in the phenolic form (I), but partly in the tautomeric diketo form (II)
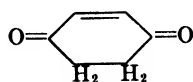
(I)   (II)

TABLE XV

| Solute | Formula | Dissolved in 100 g. water (20°C.) | |
		Grams	Moles
Benzene......................	C_6H_6	0.072	0.00092
Phenol.......................	C_6H_5OH	9.06	0.096
Pyrocatechol.................	$C_6H_4(OH)_2$ o	45.1	0.415
Resorcinol...................	$C_6H_4(OH)_2$ m	103.0	0.936
Hydroquinone.................	$C_6H_4(OH)_2$ p	7.2	0.0654
Pyrogallol...................	$C_6H_3(OH)_3$	44.4	0.352
Toluene......................	$C_6H_5CH_3$	0.047	0.0005
o-Cresol.....................	$C_6H_4CH_3OH$	2.45	0.023
m-Cresol.....................	$C_6H_4CH_3OH$	2.18	0.020
p-Cresol.....................	$C_6H_4CH_3OH$	1.94	0.018

The ability of the phenolic OH group to promote solubility is also apparent in the hydroxybenzaldehydes; all of them are more soluble than the parent benzaldehyde. A comparison of the solubility of these three isomers in water and organic solvents
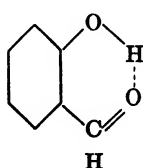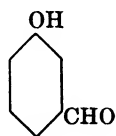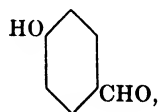
(I)   (II)   (III)

is of interest. Sidgwick and Allot[27] found that the *ortho* compound (I) is far less soluble in water than the *meta* (II) and *para* (III) compounds, whose solubilities are approximately equal. On the other hand, the *ortho* compound is the most soluble in benzene. The probable reason is the inner complex character that, according to the coordination formula (I), applies only to the *ortho* compound, which can thus form a six-membered ring. *o*-Hydroxybenzaldehyde (salicylaldehyde) is more soluble in water than benzaldehyde. This characteristic, along with

[27] N. Sidgwick and E. Allot, *J. Chem. Soc.* **123**, 2819 (1923).

the coordination ability of its phenolic hydrogen atom, is responsible for the use of salicylaldehyde as a precipitant in detecting and quantitatively determining hydrazine.[28]   All aromatic aldehydes condense with hydrazines, to produce water-insoluble aldazines (I).   As a reagent, benzaldehyde has the disadvantage that it must be used in alcoholic solution, whereas salicylaldehyde, thanks to its OH group, is sufficiently watersoluble.   It forms salicylaldazine

R—CH=N—N=CH—R
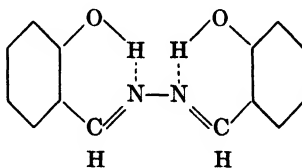
(I)   (II)

which, in conformity with its inner complex structure, (II), is less soluble in water than the analogous benzaldazine.   Accordingly, salicylaldehyde is a better reagent than benzaldehyde.   If *m*- or *p*-hydroxybenzaldehyde are considered as reagents, it is true that they have a particularly good water-solubility, but the solubilizing OH groups are retained, and continue to be active in the respective aldazines.   Consequently, only salicylaldehyde meets the dual requirements of providing a quite soluble reagent, and of producing a sufficiently insoluble aldazine.

The solubility anomalies due to inner complex binding are not unique with *o*-hydroxybenzaldehyde.   Sidgwick[29] found that abnormal solubilities are always displayed by organic hydroxy compounds (alcohols, phenols, enols) if a CO, NO_2, or N=N group is in the α or *ortho* position to the OH group; *i.e.*, in general, if there is the possibility of an innermolecular H bridge.   For instance, *o*-nitrophenol is more difficultly soluble in water and more easily soluble in petroleum ether than the isomeric *m*- and *p*-compounds.   The same is true for the analogous solubility relationships, in these same solvents, of acetylacetone in its enol and keto forms.   It should be mentioned here, that Berg[30] found 8-hydroxyquinoline is much less soluble than quinoline (0.05 g. as against 6 g. in 100 ml. of water).   If a free uninfluenced OH group were present in 8-hydroxyquinoline, there would be no reason for a decrease in solubility; rather an increase could be expected because of the phenolic OH group.   Actually, however, neither 8-hydroxyquinoline (I) nor *o*-nitrophenol (II), nor acetylacetone (III) contains free and completely uninfluenced OH groups.   Therefore, as the following coordination formulas

[28] F. FEIGL and R. SCHWARZ, *Rec. trav. chim.* **58**, 474 (1939).

[29] N. SIDGWICK, *J. Chem. Soc.* **135**, 527 (1934); **127**, 907 (1925).

[30] Compare R. BERG, Das *o*-Oxychinolin "Oxin." Stuttgart, 1935.

show, these materials should be regarded as inner complex compounds produced by the auxiliary valence activity of the H atom of an OH group toward *ortho-* or *α*-situated nitrogen or oxygen atoms:
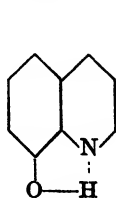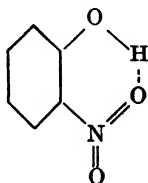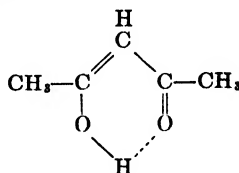
(I)   (II)   (III)

An interesting fact brought out in Table XVI is that the replacement of oxygen by sulfur in compounds of the same structure is always accompanied by a lowering of the solubility in water. This obviously may be ascribed to the facts that this replacement diminishes the similarity to water and that the sulfur atom has a lesser capacity than the oxygen atom for binding water.

TABLE XVI

Solute	Formula	Dissolved in 100 g. water (20°C.)	
		G.	Moles
Urea................	$OC(NH_2)_2$	104.7	1.75
Thiourea..........	$SC(NH_2)_2$	9.1	0.12
Phenol...............	C_6H_5OH	9.06	0.096
Thiophenol.....	C_6H_5SH	Insoluble	
Alcohol..........	C_2H_5OH	Miscible	
Ethyl mercaptan...	C_2H_5SH	Very slightly soluble	
Allyl alcohol.........	$H_2C=C_2H_3OH$	Miscible	
Allyl mercaptan.............	$H_2C=C_2H_3SH$	Insoluble	
Ethyl ether................	$C_2H_5OC_2H_5$	8.5	0.115
Ethyl sulfide..............	$C_2H_5SC_2H_5$	Insoluble	

The nitrogen atom of an NH_2 group can be regarded as a particularly active addition center for the binding of water molecules; therefore, the amino group can act as a promoter for the solubility of organic compounds. This becomes evident if the solubilities of benzene and naphthalene are compared with those of their amino derivatives. Both aniline and naphthylamine are incomparably more soluble than their corresponding hydrocarbons, and the solubility rises still more with an increased number of NH_2 groups. Several very instructive instances can be cited among aliphatic amino compounds. Thus acetic acid possesses a coordination center for the association of water molecules in

its ionogenically bound carboxyl hydrogen atom; it is miscible in all proportions with water. The esters of acetic acid do not have this coordination center, and consequently none of them are soluble in water. On the other hand, the esters of aminoacetic acid, *e.g.*, $CH_2(NH_2)\cdot$-$COOC_2H_5$ and $CH_2(NH_2)\cdot COOC_6H_5$, are quite soluble in water, because the nitrogen obviously can function as a coordination center for the association of water.

It is also noteworthy that the esters of α-amino acids, in which there is an inner molecular association (coordination) of the carboxyl hydrogen with the nitrogen, are more soluble than the free acids. In the acids, the coordination positions for a hydration are blocked by the auxiliary valence action of the nitrogen, but in the esters these are freed. The following comparisons of the solubility of the acids and their esters elucidate this point.

Aminoacetic acid

CH_2CO_2H	$CH_2CO_2C_2H_5$
H_2N ----------	H_2N
1 in 4.5 parts water	miscible with water

Iminodiacetic acid

$$CH_2\text{—}CO_2H$$
$$HN\text{----------}$$
$$CH_2\text{—}CO_2H$$
1 in 40 parts water

$$CH_2\text{—}CO_2C_2H_5$$
$$HN$$
$$CH_2\text{—}CO_2C_2H_5$$
miscible with water

Aspartic acid

$$CO_2H$$
$$CH\text{—}NH_2$$
$$CH_2$$
$$CO_2H$$
1 in 200 parts water

$$CO_2C_2H_5$$
$$CH\text{—}NH_2$$
$$CH_2$$
$$CO_2C_2H_5$$
easily soluble

Nicotinic acid

COOH / N   difficultly soluble

$COOC_2H_5$ / N   easily soluble
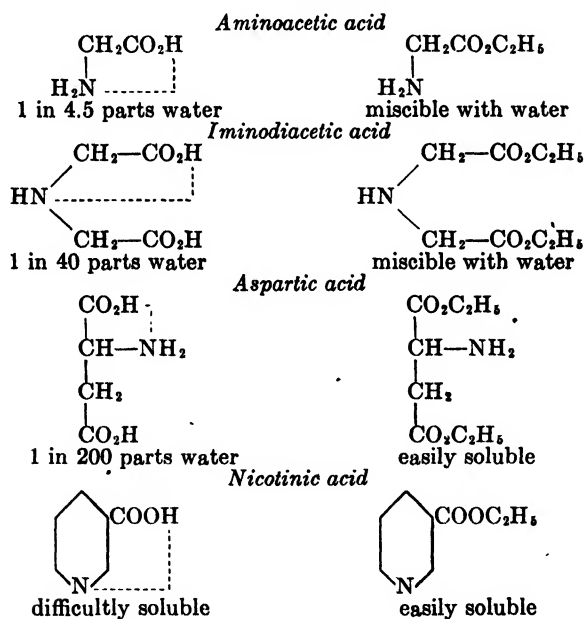
A further important fact is that the replacement by alkyls of the hydrogen atoms of an NH_2 group in organic compounds does not lower, but raises the solubility in water. This patently is because such introduction promotes hydration. The increase in the basicity of the amino group on the introduction of radicals also supports this view. The following examples show the great differences in the solubilities of amino-carboxylic acids and their N–alkylated derivatives.

Iminodiacetic acid

$$HN\begin{cases} CH_2COOH \\ CH_2COOH \end{cases}$$
1 in 40 parts water

$$C_2H_5N\begin{cases} CH_2COOH \\ CH_2COOH \end{cases}$$
very easily soluble in water

Taurine

$H_2N\cdot CH_2CH_2SO_3H$
1 in 40 parts water

$CH_3NH\cdot CH_2CH_2SO_3H$
easily soluble

$(CH_3)_2\cdot N\cdot CH_2CH_2SO_3H$
easily soluble

α-Aminocaproic acid

$$CH_3(CH_2)_3CH\cdot COOH \\ | \\ NH_2$$
1 in 48.8 parts water

$$CH_3(CH_2)_3CH\cdot COOH \\ | \\ NH(CH_3)$$
1 in 9.8 parts water

$$CH_3(CH_2)_3CH\cdot COOH \\ | \\ NH(C_2H_5)$$
1 in 9.3 parts water

$$CH_3(CH_2)_3CH\cdot COOH \\ | \\ N(C_2H_5)_2$$
very easily soluble in water

Aminoacetic acid

$$CH_2COOH \\ | \\ NH_2$$
1 in 4.3 parts water

$$CH_2COOH \\ | \\ NHC_2H_5$$
very easily soluble

$$CH_2COOH \\ | \\ \cdot N(C_2H_5)_2$$
hygroscopic

Aspartic acid

$$HOOC—CH—NH_2 \\ | \\ HOOC—CH_2$$
0.9 in 100 parts water

$$HOOC—CH—NHCH_3 \\ | \\ HOOC—CH_2$$
2.59 in 100 parts water

Camphaneamide

$$H_2N\cdot OC\cdot C_8H_{13}\begin{cases} CO \\ | \\ O \end{cases}$$
Difficultly soluble in boiling water

Camphanemethylamide

$$(CH_3)HN\cdot OC\cdot C_8H_{13}\begin{cases} CO \\ | \\ O \end{cases}$$
Soluble in cold water

The introduction of acidic or basic groups frequently promotes solubility of organic compounds. As a rule, a considerable supplementary increase of the solubility in water is then brought about through the formation of salts with alkalies or acids. This is apparent particularly with weak acids or bases. For instance, high atomic carboxylic acids (*e.g.*, palmitic or benzoic acid) are slightly soluble in water, but their alkali salts dissolve very readily. The same is true of high atomic bases (*e.g.*, quinoline) and their hydrochlorides. In such cases, the ion produced by the formation of the salt is particularly capable of hydration, in contrast to the original nonsalt-like compound. On the other hand, it is obvious that organic acids which form water-soluble salts because of the presence of hydratable groups will lose this ability if the hydration center is eliminated or changed by introduction of groups. Examples of this are available, and will be discussed in connection with weighting effects in Chapter IX.

All these examples lead to the conclusion that the very important

analytical properties of organic salts, namely slight solubility in water and solubility in organic media, are due to the effect of different groups. This latter characteristic, if it is independent of the solubility of the components, can perhaps be ascribed to the formation of pseudo-salts or inner complex salts.

This discussion of the effect of groups on solubility will be continued with a reference to the very interesting observations of Dubský and Spritzmann.[31] They found that, because of its imino group, imino-diacetic acid (I) can form inner complex rings. When titrated it acts toward alkali as a monobasic acid; also it forms a slightly soluble zinc salt. If the hydrogen atom of the NH group is replaced by an NO- or NO$_2$- group

$$
\begin{array}{ccc}
\mathrm{HN}\!\!<\!\!\begin{array}{l}\mathrm{CH_2COOH}\\\mathrm{CH_2COOH}\end{array} & \mathrm{ON\!-\!N}\!\!<\!\!\begin{array}{l}\mathrm{CH_2COOH}\\\mathrm{CH_2COOH}\end{array} & \mathrm{O_2N\!-\!N}\!\!<\!\!\begin{array}{l}\mathrm{CH_2COOH}\\\mathrm{CH_2COOH}\end{array}\\
(1) & (II) & (III)
\end{array}
$$
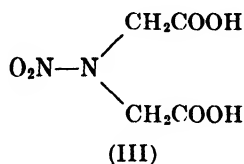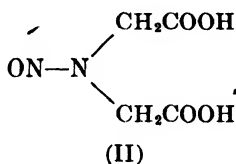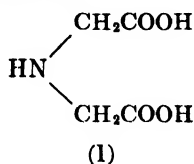
the resulting nitroso- (II) and nitroiminodiacetic (III) acids are dibasic toward alkali, and their zinc salts are quite soluble. Here, the loss of the ability to form inner complexes is thus paralleled in this instance by an increase in solubility. This remarkable relationship cannot be generalized, since soluble inner complex compounds are known in cases where inner complex anions are formed.

The loss of its coordination ability by the nitrogen of iminodiacetic acid when the imino-hydrogen is replaced by an acidic NO- or NO$_2$- group is also apparent from the behavior of the copper salts toward ammonia. The blue-green copper salt of iminodiacetic acid can add only *one* NH$_3$:

$$
\mathrm{HN}\!\!\begin{array}{c}\overset{\displaystyle\mathrm{CH_2\!-\!CO_2}}{\diagup}\\[-2pt]\text{------------------}\mathrm{Cu\cdots NH_3;}\\[-2pt]\underset{\displaystyle\mathrm{CH_2\!-\!CO_2}}{\diagdown}\end{array}
$$
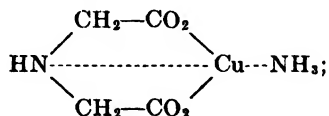
while, in contrast, the copper salts (II) and (III) can add *two* NH$_3$:

$$
\mathrm{ON\!-\!N}\!\!<\!\!\begin{array}{l}\mathrm{CH_2\!\cdot CO_2}\\\mathrm{CH_2\!\cdot CO_2}\end{array}\!\!>\!\!\mathrm{Cu}\!\!<\!\!\begin{array}{l}\mathrm{NH_3}\\\mathrm{NH_3}\end{array}
\qquad\text{and}\qquad
\mathrm{O_2N\!-\!N}\!\!<\!\!\begin{array}{l}\mathrm{CH_2\!\cdot CO_2}\\\mathrm{CH_2\!\cdot CO_2}\end{array}\!\!>\!\!\mathrm{Cu}\!\!<\!\!\begin{array}{l}\mathrm{NH_3}\\\mathrm{NH_3}\end{array}
$$

$$
(II)\qquad\qquad\qquad\qquad (III)
$$
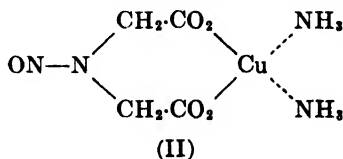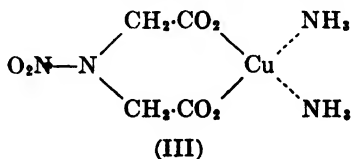
Phenyliminodiacetic acid, C$_6$H$_5$—N(CH$_2$·COOH)$_2$ because of the loss of the auxiliary valence action of the nitrogen atom, is a dibasic acid that

[31] J. Dubský and M. Spritzmann, *J. prakt. Chem.* **96**, 113 (1917).

consumes *two* equivalents of KOH when titrated. Nevertheless, its copper salt (IV) can add only *one* NH_3, probably because the C_6H_5-group is coordinated on the copper atom, forming a complex in which the Cu atom has the coordination number $= 4$:

$$N \begin{array}{c} {/}\!\!\!\!\!\!CH_2\!\!-\!\!CO_2 \\ -\!\!C_6H_5 - - - - - - -Cu - NH_3. \\ {\backslash}\!\!\!\!\!\!CH_2\!\!-\!\!CO_2 \end{array}$$

(IV)
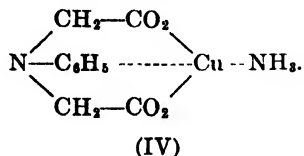
The great majority of all dissolution processes are due to a mutual action between solute and solvent, in which, as shown by the foregoing examples, constitutional factors and the activity of certain atomic groups play a role. There are, however, other dissolution processes in which the activity of a third material, present in dissolved form, inserts itself into the binary system: solute-solvent. The first observations and measurements along this line were made by Engler and Dieckhoff.[32] They found that certain hydrocarbons dissolve to a considerable extent in aqueous solutions of salts, and that cosolutes can further increase such solubility. For instance, 1 ml. of xylene dissolves in 100 ml. of warm (10%) sodium stearate solution; addition of 10 ml. of phenol raises the xylene solubility to 37 ml. The corresponding solubilities of turpentine are still more striking, namely, 0.8 ml. and 101 ml. Neuberg,[33] on the basis of numerous experiments, stated that organic and inorganic compounds which are insoluble in water in many cases are quite soluble in concentrated (25%) aqueous solutions of sodium salts of organic acids (benzoic, salicylic, benzenesulfonic, *etc.*). He suggested the term "hydrotropy" for this effect. Later, Hahn[34] showed that ethyl and propyl alcohol, acetone, and pyridine, in many cases will bring about increases in solubility equal to those due to benzoates and salicylates. Lithium iodide and triethanolamine borate have also been found to be strongly hydrotropic.[35] It is now known that hydrotropy and other essentially similar effects which promote solubilization are highly important with regard to many technical and pharmaceutical products and purposes, and also play a part in the physiological process of transporting material in the living organism.

Hydrotropy, or the process of hydrotropic dissolution, can be considered, as was solvation, from the standpoint of coordination chemistry.

[32] C. ENGLER and E. DIECKHOFF, *Arch. Pharm.* **230**, 561 (1892).

[33] C. NEUBERG, *Biochem. Z.* **76**, 107 (1916); see also C. NEUBERG and F. WEINMANN, *ibid.* **229**, 476 (1930).

[34] F. V. v. HAHN, *Kolloid-Z.* **62**, 202 (1932).

[35] Compare H. FREUNDLICH and G. V. SLOTTMANN, *Biochem. Z.* **188**, 101 (1927).

According to these concepts, a complex compound (solvate) that has been formed by the solvation of a material and that often is stable only in solution, is by no means fully saturated with respect to its valence or molecular binding forces. Consequently, certain suitable portions of a solvate may be expected to permit a further coordinative association of compounds that of themselves are incapable of solvation. In this way, the solvate, to a degree, becomes the carrier responsible for the solubility of the coordinated compound. It must be remembered that these complex compounds between the solvate and hydrotropically dissolved materials need not be isolable; they may be no more than loose unions of the components and stable only in solution. The significance of this effect is clearly displayed in the behavior of freshly precipitated beryllium hydroxide toward concentrated solutions of normal beryllium salts. Parsons[36] found that about 3 equivalents of $Be(OH)_2$ are dissolved by beryllium oxalate or sulfate; the chloride dissolves about 4 equivalents, and the acetate around 6. Dilution of these solutions causes the $Be(OH)_2$ to precipitate, but not completely. Complex compounds could not be isolated from the solutions, nor was there evidence of the production of an hydrosol. The behavior of beryllium salts toward $Be(OH)_2$ can be taken as a model instance of hydrotropism. Hydrotropic actions are also of practical significance in systems of compounds that differ greatly in their chemical composition.

The following increases in solubility, at room temperature, of compounds, that by themselves are not more than slightly water-soluble, will be considered from this standpoint. Hippuric acid dissolves in water to the extent of 0.37%; in 1 N sodium formate or acetate solution, the solubility increases to 1% and 1.75%, respectively.[37] The solubility of caffeine in water is 1.46%; in 0.1 N sodium salicylate it is 4.4%.[38] In the presence of 79 g. of sodium benzoate, 100 ml. of water will dissolve as much as 58 g. of caffeine.[39] Certain higher (water-insoluble) alcohols dissolve readily in water solutions of their monosulfonic esters.[40] It should be further pointed out that the solubility (0.005%) of uric acid in water is raised by proteic acids,[41] and that water solutions of the alkali salts of desoxycholic acid have great solvent ability for a wide variety of organic compounds.[42] The foregoing instances show that it is clearly the organic anions that are to be looked on as the vehicles of hydrotropic

[36] C. L. PARSONS, *J. Phys. Chem.* **11**, 651, 659 (1907).

[37] E. LARSON, *Z. physik. Chem.* **127**, 233 (1927).

[38] K. ZIPF, *Z. physiol Chem.* **187**, 240 (1930).

[39] M. CHAMBON, *J. pharm. chim.* **26**, 216 (1937).

[40] H. PRINS, *Rec. trav. chim.* **42**, 25 (1923).

[41] K. YABARA, *Biochem. Z.* **213**, 456 (1929).

[42] H. WIELAND and H. SORGE, *Z. physiol. Chem.* **97**, 1 (1916).

solubility. This function can also be exercised by neutral molecules and by cationic constituents of compounds. This is exemplified by the increased water-solubility of camphor, sulfonal, and pyramidone on the addition of urethanes; the increased solubility of aniline in the presence of aniline salts,[43] and the considerably higher solubility of aniline, m- and p-toluidine, quinoline, and p-aminoazobenzene in ammonia[44] as compared with pure water. Smith,[45] in a study which is important with respect to hydrotropy, showed that many organic liquids of the most divergent chemical types are much more soluble in aqueous soap solutions than in water. A partial salting out sometimes occurs. It has been observed that the organic substances added to increase the solubility cannot subsequently be completely removed by extraction with organic liquids, such as ether. Smith found that sodium oleate promotes solubility to a particularly striking extent. Some of his findings are shown in the following table.

TABLE XVII

Solute	Solubility (g.) in 100 g.		Relation of normal: hydrotropic solubility (approximate)[a]
	Water	0.4 N Na-oleate	
Aniline................. ..	3.61	11.5	1:3.5
Ethyl benzoate........	0 08	5.4	1:75
Benzene..........	0.17	4.0 (11.9)	1:27 (1:74)
o-Cresol..................	2.45	37.6	1:17
Cyclohexanol...............	6.0	59.0	1:11
Hexane...................	0.014	2.4 (7.3)	1:185 (1:560)
Isoamyl alcohol..............	2.8	58.0	1:21.5
Methyl acetate..............	32.19	71.0	1:2.5
Nitrobenzene...............	0.18	4.32	1:27
Toluene..................	0.044	3.5 (11.4)	1:87 (1:285)

[a] In calculating the relation normal: hydrotropic solubility, account was taken of the fact that 100 ml. of 0.4 N sodium oleate contain 10.8 g. of this salt.

The particularly large effect of sodium oleate in the hydrotropic solubilization of these materials may possibly be due to the carbon double bond in the oleate anion, which may serve as a center for the addition of the materials that are only slightly soluble in water. The solubility values enclosed in parentheses have a special interest. They were not obtained by dissolving the particular materials (benzene, hexane, toluene, etc.) directly in 0.4 N sodium oleate solution, but by mixing the

[43] H. v. EULER and O. SVANBERG, Z. Elektrochem. 23, 192 (1917).
[44] F. FEIGL, unpublished studies.
[45] E. L. SMITH, J. Phys. Chem. 36, 1401, 1672 (1932).

material with oleic acid, and then treating the mixtures with the quantity of sodium hydroxide calculated to just neutralize the oleic acid. The solution was thereupon diluted with water to 0.4 N. The solubility increments thus obtained indicate that the loose unions formed between the sodium oleate (or the oleate ion) and the hydrotropically dissolved material, differ according to the particular conditions attending their formation. The semicolloidal nature of concentrated soap solutions doubtless connect these cases with colloidal solutions and to the action of protective colloids (see Chapter X). Such relationships are important to the detergent action of soap solutions in which an important part is played by the solubilization of organic materials by dilute soap solutions.[46]

Hydrotropic solution, according to the ideas advanced here, is primarily due to the association of compounds that are incapable of hydration with hydrates that are already present. In most cases, it cannot be stated with certainty which constitutional peculiarities of the ligands are responsible for the additional solubility. The term hydrotropic can be used appropriately for all cases of anomalous solubility that cannot be ascribed to the formation of detectable stoichiometrically defined complex compounds. There is a possibility that the frequent impairment of the sensitivity of precipitation reactions by apparently indifferent materials belongs to this class of phenomena. Hydrotropic phenomena are probably closely allied to colloidal phenomena[47] which will be discussed in Chapter X.

The preceding discussion shows that the process of dissolution of a material in a solvent from which it subsequently can be recovered unchanged may be regarded as a chemical reaction leading to the formation of molecular compounds between solvent and solute. Here, as in the phenomenon of hydrotropy, an important role is played by the presence of certain atomic groups, or more correctly, of certain atoms that can be coordinated. These groups or atoms are contained in the molecules of solvent, solute, or the hydrotropic agent. Likewise, a constitutional similarity of the molecular species involved is significant. However, this statement should be somewhat qualified as it has not yet been determined whether the coordinative chemical viewpoint adopted here will apply to all solution processes. It appears that it is more justified in the dissolution of solids in indifferent liquids than for the process of dissolving liquids in each other. The formation of stoichiometrically defined molecular compounds has been established with

[46] J. W. McBAIN, through his classic studies, has placed "the chemistry of soaps" on a new foundation. See his "Solubilization and Other Factors in Detergent Action" in *Advances in Colloid Sciences*. New York, 1942.

[47] Compare A. CHWALA, *Kolloidchem. Beihefte* **31**, 222 (1930).

certainty in many mixtures of liquid components. (The same holds for melts.) However, the union of liquid phases (particularly those of like densities and of great chemical similarity) in which, in contrast to the solution of solids, doubtless much less work of distribution must be accomplished, can also be regarded as a purely physical process of mixing. This holds especially for liquids that are miscible in all proportions, and for which, therefore, the terms solvent and solute have no concrete meaning.[47a] With reference particularly to the solution of solids in indifferent solvents, and to the activity of solvent mixtures, it should be pointed out that consideration should be given to the state of the molecules of a solvent or a solvent mixture. It is quite clear that polymerates of molecules can behave differently than single molecules. A pertinent illustration is the fact[48] that $HgCl_2$, HgI_2, and $CoBr_2$ are quite soluble in acetaldehyde, but only slightly soluble in paraldehyde (i.e., in trimeric CH_3CHO). Other salts such as $LiCl$, $FeCl_3$, and $SbCl_3$, show no such solubility differences. The special molecular structures of the solvent and solute undoubtedly have a great effect on the solubility. The same is true of the dielectric constant of a solvent, its viscosity, and the related diffusibility of a dissolved material. Furthermore, in solution processes that lead to an equilibrium, consideration must be given to the state of the dissolved material, i.e., to the degree to which it is dissociated or polymerized in solution. As to the latter, it is necessary to take into account, not only polymers which can be detected by osmotic measurements or effects, but also loose molecular aggregates, i.e., "molecular swarms" which may be present. It can be maintained, therefore, that the principle of group action, based on the conceptions of coordination chemistry, does not provide an "explanation" of solution processes, but merely place an important partial phenomenon in the foreground of the discussion. In the following chapter it will be shown that the assumption of group action clarifies many phenomena of solution that have been ascertained experimentally, and that this point of view is a valuable guide for studies in the field of reaction specificity and selectivity.

This chapter has dealt with group actions as they affect solubilities of compounds. The discussion can be appropriately concluded by considering an interesting rule that has been evolved from a survey of the behavior of inner complex salts toward organic solvents. It was pointed out in Chapter III that inner complex salts frequently exhibit an abnormal color or solubility or both. Abnormal solubilities are encountered with respect to water as well as toward organic liquids. Often, excellent solubility in organic liquids is regarded as a characteristic mark

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[47a] By convention, the liquid having the greater mass is called the solvent.

[48] Cited from P. WALDEN op. cit., p. 455.

of inner complex salts.   However, this statement, in so general a form, is not correct.   By no means are all inner complex salts soluble in organic liquids, nor do all of the latter show a uniform behavior with respect to their dissolving power for inner complex salts.[49]   Furthermore, various metal salts of a given complex-former may behave quite differently toward a particular organic solvent.[50]

Chloroform seems to occupy a special place among organic liquids; its solvent powers for inner complex salts are strikingly high.   If the behavior of such salts toward this liquid is examined, a regularity will be discovered, which doubtless can be attributed to group action.   Table XVIII contains some qualitative findings with typical inner complex salts.

An inspection of the table reveals that *excellent solubility in chloroform is a characteristic of only those inner complex compounds whose molecules contain no free acidic or basic groups* (Nos. 1, 4, 5, 6, 8, 11, 12, 16, 17).   The antagonism of such groups to chloroform-solubility is exhibited by Nos. 2, 3, 7, 9, 10, 13, 14, 15, 18.   In these cases, as shown by the coordination formulas of the inner complex salts, the free acidic or basic groups are assumed to include also those that participate in inner molecular ring closures through the auxiliary valence activity of certain of their atoms.   The responsibility of free acid groups for the insolubility in chloroform is definitely shown by a comparison of the behavior of inner complex salts of dimethylglyoxime and salicylaldoxime with the corresponding inner complex salts of the monoxime ethers (No. 3 *vs.* 4, 15 *vs.* 16, 17 *vs.* 18).   The etherification, *i.e.*, the replacement of the acidic hydrogen of the free NOH group by a methyl group, results in ready chloroform-solubility of the respective inner complex salts.   The assumption that solubility in chloroform is hindered by acidic groups in inner complex salts agrees with the fact that inner complex salts of the nitrosonaphthols are very soluble, whereas those of the sulfonated nitrosoanaphthols are completely insoluble (Nos. 8, 9, 10).   The same influence of the sulfonic group appears if Nos. 6 and 7 are compared.

This solubility rule, which is announced here tentatively, has been found to hold in eighteen typical cases.   Obviously it will have to be tested in many other instances, and above all it must be subjected to

[49] Few quantitative data on the solubility of inner complex salts in various organic solvents have been available up to now.   Comparative values with the solubilities of the organic components of inner complex salts are practically nonexistent.   Such figures would have great theoretical and practical value in extending and deepening the knowledge of inner complex salts and solution processes.

[50] Compare in this connection the statements in Chapter VI regarding the solubility of inner complex salts of *o*-nitrosophenol and thionalid in certain organic liquids.

[51] It may certainly be expected that the extent of the effect of acidic or basic groups (or perhaps of polar groups generally) in lowering the chloroform-solubility of inner

TABLE XVIII
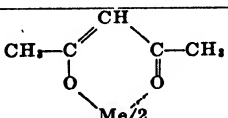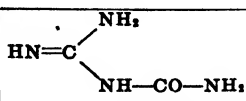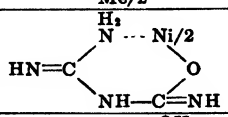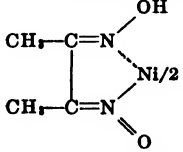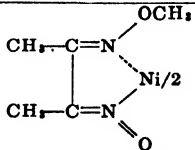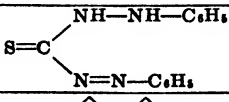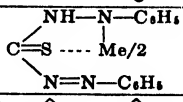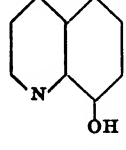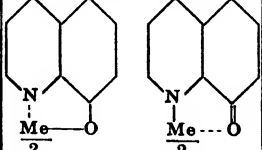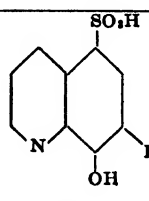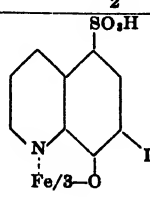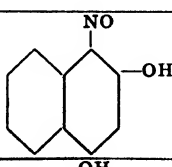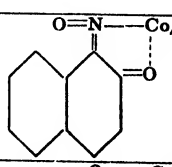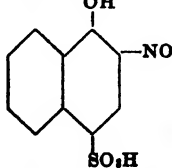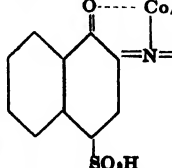
No.	Inner complex-forming compound		Coordination formula of inner complex salt	Solubility in chloroform
	Name	Formula		
1	Acetylacetone	$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$	$\begin{array}{c} CH \\ CH_3-C \quad C-CH_3 \\ O \qquad O \\ Me/2 \end{array}$	Very soluble
2	Dicyandiamidine, compare page 205	$\begin{array}{c} NH_2 \\ HN=C \\ NH-CO-NH_2 \end{array}$	$\begin{array}{c} H_2 \\ N \cdots Ni/2 \\ HN=C \qquad O \\ NH-C=NH \end{array}$	Insoluble
3	Dimethylglyoxime, compare page 270	$\begin{array}{c} CH_3-C=NOH \\ CH_3-C=NOH \end{array}$	$\begin{array}{c} OH \\ CH_3-C=N \\ \quad\quad Ni/2 \\ CH_3-C=N \\ O \end{array}$	Slightly soluble
4	Dimethylglyoxime monomethylether, compare page 271	$\begin{array}{c} CH_3-C=NOCH_3 \\ CH_3-C=NOH \end{array}$	$\begin{array}{c} OCH_3 \\ CH_3-C=N \\ \quad\quad Ni/2 \\ CH_3-C=N \\ O \end{array}$	Very soluble
5	Diphenylthiocarbazone, compare page 241	$\begin{array}{c} NH-NH-C_6H_5 \\ S=C \\ N=N-C_6H_5 \end{array}$	$\begin{array}{c} NH-N-C_6H_5 \\ C=S \cdots Me/2 \\ N=N-C_6H_5 \end{array}$	Very soluble
6	8-Hydroxyquinoline, compare page 181	(structure, quinoline with OH)	(structure, quinoline complex Me/2)	Very soluble
7	7 Iodo-8-hydroxy-quinoline-5-sulfonic acid, compare page 187	(structure, SO_3H, I, OH)	(structure, SO_3H, I, Fe/3-O)	Insoluble
8	Nitrosonaphthol 1,2 or 2,1, compare page 252	(structure, NO, OH)	(structure, O=N—Co/3, O)	Very soluble
9	Nitrosonaphthol-4-sulfonic acid compare page 258	(structure, OH, NO, SO_3H)	(structure, O—Co/3, N=O, SO_3H)	Insoluble

TABLE XVIII (*Continued*)

No.	Inner complex-forming compound		Coordination formula of inner complex salt	Solubility in chloroform
	Name	Formula		
10	Nitrosonaphthol-3,6-disulfonic acid, compare page 258	NO, OH, HO₃S, SO₃H	O=N—Co/3, O, HO₃S, SO₃H	Insoluble
11	Nitrosophenol, compare page 260	NO, OH	N=O, Me/2, O	Very soluble
12	Nitrosophenyl-hydroxyl-amine, compare page 262	N—OH, NO	N, O, N, Me/2, O	Very soluble
13	Quinaldinic acid compare page 221	N, COOH	N, C, O, Me/2—O	Insoluble
14	Rubeanic acid, compare page 248	H₂N—C—C—NH₂, S, S	HN=C, C=NH, S, S, Me	Insoluble
15	Salicylaldoxime, compare page 266	CHNOH, OH	H, C, N—OH, Cu/2, O	Slightly soluble
16	Salicylaldoxime-methyl ether, compare page 197	CHNOCH₃, OH	H, C, N—OCH₃, Cu/2, O	Very soluble
17	Salicylaldehyde	OH, CHO	O, Cu/2, O, C, H	Very soluble
18	Salicylaldoimine	OH, CHNH	O, Cu/2, NH, C, H	Insoluble

quantitative inspection.[51]   If it should turn out to be generally applicable, it will certainly prove very useful.   Even now, it may be stated with considerable assurance that the introduction of SO_3H groups, to induce water-solubility in organic reagents, will be accompanied by a loss of solubility of their salts in organic liquids, and hence a decrease or actual loss of the possibility of extracting such products from aqueous solutions or suspensions.   It may be expected that any blocking of acidic groups by esterification or etherification, or the changing of basic NH_2 groups by alkylation, will promote the solubility of the inner complex salts in organic liquids.

 · A knowledge of the effects of groups on the solubility of inner complex salts in organic solvents will be of analytical import when it is desired to bring about certain improvements by modifying the constitution of inner complex-forming reagents, or when the intent is to secure the extractability or flotation of inner complex salts with organic liquids.   A further use of this solubility rule in the elucidation of the constitution of inner complex salts and in clarifying the function of certain groups in organic reagents was discussed in Chapter VII.

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complex salts will depend on the nature of the respective groups.   Even Table XVIII shows that the NOH group doubtless has less effect than the SO_3H group.   Furthermore, any water content of the inner complex salts, and also the valence of the metal atoms, may play a part.   Any extended study of the solubility rule must take these factors into account.   A survey of the instances that comply with the rule, and likewise of those that depart from it, will surely be quite informative in gaining an understanding of this province of the important phenomenon of solubility.

The Influence of Size—and Weighting—Effects on Solubility and Salt-Forming Ability

Several important regularities concerning the solubility of solids in organic solvents and water were given in the preceding chapter. These effects could be ascribed to the presence and activity of certain atomic groups. The solubilities of compounds that function as reagents, or that are formed as reaction products, are highly important for analytical purposes.[1] In general, it is much more desirable that reagents be soluble in water than in organic solvents because the reaction medium in chemical analyses is generally a water solution. Consequently, the addition of alcohol or acetone solutions of reagents sometimes causes undesirable complications because of the precipitation of a water-insoluble reagent or mineral cosolutes. In qualitative analysis, it is often an advantage if reaction products, that are either soluble or insoluble in water, will dissolve in organic solvents that are not miscible with water. It is then possible to subject the aqueous system to an extraction or a flotation.[1a] Usually this procedure improves the perceptibility of small quantities of materials, particularly of colored compounds. When reaction products cannot be extracted, or if they do not lend themselves to flotation, it is desirable that they dissolve to not more than a slight extent in water. There is no strict proportionality between the solubility and the perceptibility of a precipitated material (see Chapter II), but it obviously is advantageous to produce materials that are only slightly water-soluble. Another factor of importance in analytical work is the relation between the water-solubility of a material and its vulnerability to attack by aqueous solutions of acids, alkalies, and other reagents. In chemical solution processes, *i.e.*, those that proceed because of decomposition, it is the portions of the solid that are present in water solution which take part in ionic reactions. This means that the following equilibria must be considered when dealing with a slightly soluble compound:

$$AB \rightleftharpoons AB \rightleftharpoons A^+ + B^-$$
$$\text{(solid)} \qquad \text{(dissolved)}$$
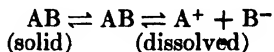
Reactions with H^+, OH^-, and other ionic species may occur with the ionic species, A^+ or B^-, that are formed when the solid dissolves in water.

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[1] As in Chapter VIII, no account is taken here of the influence of the free surface of a solid on its solubility. The relations between particle size and solubility will be discussed in Chapter X.

[1a] Concerning analytical flotation see Chapter X.

In this sense, every chemical solution of a solid proceeds through those parts of the solid that dissolve and then dissociate in water, and that are constantly replenished as they are consumed. Accordingly, the more soluble a solid is in water, the greater will be its chemical assailability by dissolved reagents.[2]

The solubility of organic compounds in water is associated with the presence, in the molecule, of groups that can be hydrated. Consequently, the water molecules can attach themselves to these groups, and thus alter the character of the anhydrous material in proportion to the number so attached. In extreme cases, the character of a compound which is thus highly hydrated will approach that of water; so in this sense it is legitimate to speak of a "water similarity," which brings about or increases the solubility in water. It is clear that this effect can be obtained more easily and more completely when the water-free molecule is small and light, since a group acting as a hydration center cannot make a large molecule as thoroughly similar to water (and therefore water-soluble) as it can a small one. Accordingly, the water solubility of organic compounds of a given type must decrease with increasing molecular weight. The following compilation shows how the increased water-solubility brought about by the OH or COOH groups is diminished in homologous series of primary alcohols and monocarboxylic acids by weighting the alcohol or the acid molecule. The solubility figures are the grams that dissolve in 100 g. water at 20–25°C.

$CH_3 \cdot CH_2 \cdot OH$	∞	$CH_3 \cdot COOH$	∞
$CH_3 \cdot (CH_2)_2 \cdot OH$	∞	$CH_3 \cdot CH_2 \cdot COOH$	∞
$CH_3 \cdot (CH_2)_3 \cdot OH$	∞	$CH_3 \cdot (CH_2)_2 \cdot COOH$	55.4
$CH_3 \cdot (CH_2)_4 \cdot OH$	8.5	$CH_3 \cdot (CH_2)_3 \cdot COOH$	3.4
$CH_3 \cdot (CH_2)_5 \cdot OH$	0.59	$CH_3 \cdot (CH_2)_4 \cdot COOH$	1.08
$CH_3 \cdot (CH_2)_6 \cdot OH$	0.18	$CH_3 \cdot (CH_2)_5 \cdot COOH$	0.22

This effect can also be seen by contrasting hydroxyacetic acid with its derivatives in which the hydrogen of the alcoholic OH group is replaced by alkyl or aryl groups:

$HO \cdot CH_2 \cdot COOH$, miscible with water
$CH_3O \cdot CH_2 \cdot COOH$, easily soluble in water
$C_2H_5O \cdot CH_2 \cdot COOH$, easily soluble in water
$C_6H_5O \cdot CH_2 \cdot COOH$, 1 part soluble in 10 parts water
$C_{10}H_7O \cdot CH_2 \cdot COOH$, difficultly soluble in water.

Weighting effects can likewise be observed in aromatic compounds.

[2] In dealing with compounds that are only slightly soluble in water, it is necessary also to assume a direct reactivity of the molecules or ions that are still present in the solid lattice. Evidence for this is the reactive ability of solids in the absence of solvents (compare J. A. HEDVALL, op. cit. on p. 647), as well as the fact that when solution of materials in water results in the formation of hydrates, the process always begins at the solid-water interface. The importance of the surface of solids for chemical processes is discussed in detail in Chapters X and XI.

The table on p. 396 shows that all cresols are less water-soluble than phenol, as a result of the inclusion of a CH_3 group in the phenol molecule. A comparison of the solubilities of benzoic acid and β-naphthoic acid, and of aniline and α-naphthylamine, in 100 g. of water at 20°C.,

—COOH	—COOH	NH₂	NH₂
0.29 g.	0.006 g.	3.6 g.	0.17 g.
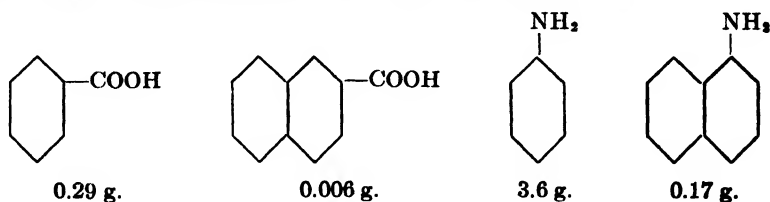
demonstrates that a characteristic decrease in the water-solubility of comparable aromatic compounds occurs with increasing molecular weight and size.

Lowering the solubility of organic compounds by weighting the molecule is important with respect to organic reagents. In many cases, this effect makes it possible to decrease very considerably the solubility of the salts formed in precipitation reactions with consequent rise in the sensitivity of these reactions. Such weighting increases the sensitivity not only through lowering the solubility, but also because an increase in the molecular volume often makes the precipitates more visible. The fact that weighting lowers the solubility not only of the precipitable salts but also of the reagent is no disadvantage, because the acids and bases used as reagents can, as a rule, be employed in alcoholic solution, or in the form of their quite water-soluble alkali salts or hydrochlorides.

Table XIX shows the lowering of solubilities of salts of organic acids by weighting effects. These data were determined by Ephraim.[3]

TABLE XIX

Metal	Normality of the saturated salt solution			
	Benzene sulfonate	Naphthalene 2-sulfonate	Anthracene 1-sulfonate	Anthracene 2-sulfonate
Ca............	1.74	0.0437	0.00048	0.00028
Ba............	0.319	0.0069	0.00105	0.00007
Zn............	0.375	0.0096	0.00086	0.00013

The solubility of the Ca, Ba, and Zn salts of these aromatic sulfonic acids decreases quite considerably with increasing molecular weight of the acid. This is true also for a series of other salts. The fact that the salts of anthracene-2-sulfonic acid are all less soluble than those of the isomeric 1-acid shows that there are specific constitutional effects in addition to the unspecific weighting effect.

[3] F. EPHRAIM, *Helv. Chim. Acta* 8, 229 (1925).

The preceding comparison shows clearly the influence of the weighting effect of the radicals bound to the salt-forming SO_3H group.[4] As noted on p. 11, the sensitivity of a precipitation does not necessarily parallel the insolubility of the particular precipitation products. Consequently, in determining weighting effects that can be used analytically it is more appropriate to compare precipitation sensitivities, or their corresponding identification limits, rather than solubilities. Such comparisons can be made in test tubes or as spot reactions. In both techniques, an increase in sensitivity will be evident if weighting effects are active. In this way, Tamchyna[5] detected a weighting effect in the reaction of alkali xanthates with molybdate or copper. Alkali xanthates of the general formula (I) containing various radicals (R) are readily available. Compounds of the type (II) are produced by reaction with molybdates, whereas copper salts form cuprous xanthate (III), along with dixanthate, i.e., compounds of an entirely different structure:

$$S=C\diagup^{SNa}_{\diagdown OR} \qquad MoO_3 \cdot SC(SR)OH \qquad S=C\diagup^{OCu}_{\diagdown SR}$$

$$\begin{array}{ccc} \text{(I)} & \text{(II)} & \text{(III)} \\ \text{colorless} & \text{red-violet} & \text{yellow} \end{array}$$
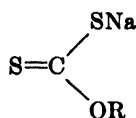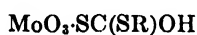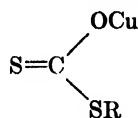
If R = ethyl, butyl, isoamyl, cetyl, myricyl, or cellulose, i.e., radicals with progressively increasing weight, there is no difference in the color of the products, but the sensitivity of the test reaction increases decidedly as the weight of the radical increases.

Berg and Roebling[6] furnished a very instructive instance of the weighting effect of certain groups on the solubility of metal salts of organic acids. They studied the inner complex salts of thioglycolic acid and of its anilide and α-naphthylamide. These inner complex salts have the coordination formulas:

$$\begin{array}{ccc} \text{(I)} & \text{(II)} & \text{(III)} \end{array}$$
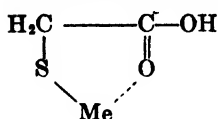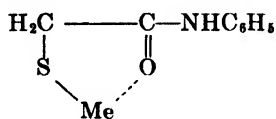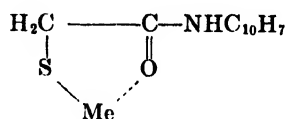
While only the Cu, Ag, and Au salts (I) of thioglycolic acid are stable in mineral acid solution, the stability in the case of the anilide complex

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[4] Weighting effects are also encountered in the formation of salts of amino acids with aromatic sulfonic acids. The formation of these salts has been studied extensively by M. BERGMANN and his co-workers [J. Biol. Chem. 129, 609 (1939); 135, 487 (1940); 143, 121 (1942)] for the isolation and characterization of amino acids.

[5] J. TAMCHYNA, Mikrochemie 9, 229 (1931).

[6] R. BERG and W. ROEBLING, Ber. 68, 403 (1935).

includes the salts of Cu, Ag, Au, Hg, Sn, As, Sb, Pt, and Pd (II).   The salts (III) of the naphthylamide of thioglycolic acid are still more stable toward acid and heat.   The decreasing solubility of the salts shows the weighting effect of the anilide and naphthylamide groups in salts of thioglycolic acid.   Precipitations from 0.2 N mineral acid solutions can be made at the following dilutions:

	Thioglycolic acid	Anilide	α-Naphthylamide
Cu................	1: 200,000	1:4,000,000	1:10,000,000
Ag...................	1:1,000,000	1:3,000,000	1: 5,000,000
Au...................	1: 500,000	1:1,000,000	1: 2,500,000

A characteristic weighting effect is seen if the inner complex salts of 8-hydroxyquinoline, of 5,7-chloro-8-hydroxyquinoline, and of 5,7-bromo-8-hydroxyquinoline are compared:

(Me = 1 equivalent of metal)

(I)   (II)   (III)
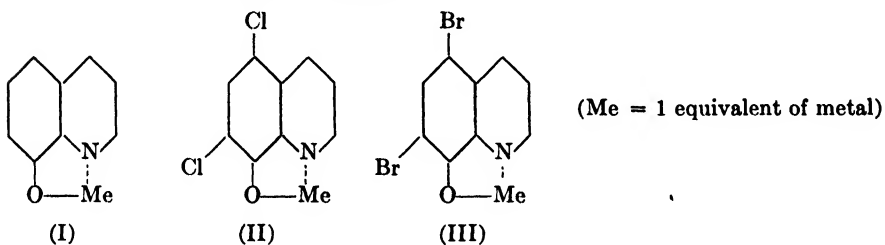
8-Hydroxyquinoline forms slightly soluble inner complex salts of the type (I), with numerous metal ions.   All of these salts, however, are stable only in neutral, alkaline, or weak acetic acid solution.[7]   In contrast, Cu, Fe, Ti, and Hg ions react with the halogen-substituted 8-hydroxyquinolines to form inner complex compounds (II) and (III) that are not soluble in dilute mineral acids.[8]   Accordingly, a weighting effect here runs parallel with a rise in the selective action of the organic reagent.[9]

The studies by Ephraim[10] on the behavior of aromatic sulfonic acids toward ammoniacal solutions of Cu, Zn, Cd, and Ni salts demonstrate weighting effects attributable to the introduction of halogen atoms. These solutions remain unaltered when ammoniacal or alkaline solutions

[7] R. BERG, Das o-Oxychinolin "Oxin."   Stuttgart, 1935.

[8] R. BERG, Z. anorg. allgem. Chem. **204**, 208 (1932); R. BERG and A. KÜSTENNACHER, ibid. **204**, 215 (1932).

[9] E. GASTINGER, Z. anal. Chem. **126**, 373 (1944), recommends 5,7-dibromo-8-hydroxyquinoline as precipitant for gallium in the presence of aluminum in acid solutions.

[10] F. EPHRAIM, Ber. **54**, 965 (1921).

of aromatic sulfonic acids are added. This means that the resulting salts $[RSO_3]_2[Me(NH_3)_4]$ are readily soluble in water. In contrast, aromatic sulfonic acids that carry chlorine, bromine, or nitro groups as substituents at any place in the molecule, form water-insoluble metal ammine salts. Consequently, a distinct weighting effect is achieved by these substitutions. No effect is observed when OH, COOH, or SO_3H groups are introduced into aromatic sulfonic acids. All of these groups are hydratable, and hence exert no weighting effect. The difference between the parent and substituted aromatic sulfonic acids is especially evident in their behavior toward $[Ni(NH_3)_4]^{++}$ ions. According to Ephraim, the precipitation of Ni-ammine salts can be used to separate halogen- and nitro-substituted monosulfonic acids from nonsubstituted admixtures, and also to separate substituted mono- and disulfonic acids.

It can be taken as a general rule that a weighting effect, with respect to solubility in water, can be exerted only by atoms and atomic groups that are not susceptible to hydration. This statement is confirmed by the foregoing examples. The introduction of hydratable atomic groups not only does not bring about a weighting effect but, in fact, they may even obliterate this effect normally conferred by other groups or atoms. This result is shown by a comparison of the properties of the iron salts of 8-hydroxyquinoline (I), 5,7-dihalogen-8-hydroxyquinoline (II), and 7-iodo-5-sulfonic-8-hydroxyquinoline (III):
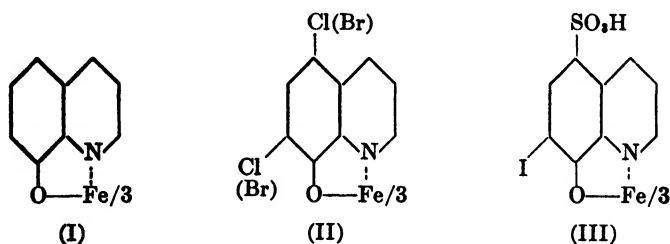
Color	Increment in weight per mole of reagent	Solubility
(I): Green-black....	0	Insoluble in water; soluble in dilute mineral acids
(II): Black-green....	70 (160)	Insoluble in water; insoluble in dilute mineral acids
(III): Green........	260	Water-soluble; stable toward dilute mineral acids

The preceding comparison shows that the essentially identical color of the inner complex salts (I), (II) and (III), is doubtless due to the fact

that they contain the same kind of inner molecular rings built up with the iron atom. Obviously, the introduction of substituents into the benzene ring of the hydroxyquinoline has not influenced the color. On the other hand, the weighting effect of the iodine atom in (III) which, from the standpoint of weight, exceeds the weighting effect of two chlorine atoms in (II) and which is only a little less than that of two bromine atoms, has not only been wiped out by the introduction of the hydratable SO_3H group, but (III), in contrast to its parent compound (I), is actually soluble in water. "Yatren," which is 7-iodo-5-sulfonic-8-hydroxyquinoline, and hence the parent of (III), has been recommended by Yoe[11] as a sensitive reagent for ferric salts. It is noteworthy that smaller quantities of iron can be detected with this reagent than with 8-hydroxyquinoline, and it offers the further advantage that it can be used in acidified solutions.

Interesting weighting effects have been found in 1,2-*anti*-dioximes, in which the C(:NOH)—C(:NOH) group exhibits a selective action toward Ni^{++}, Pd[++], and Fe^{++} ions. When this dioxime group is bound to aliphatic radicals, the properties of the corresponding ferrous salts differ from those of the ferrous salts of aromatic dioximes. This is shown in the following comparison:
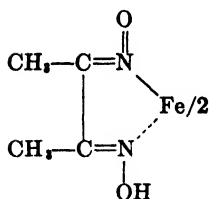
Ferrous dimethylglyoxime[12]
water-soluble
red
unstable
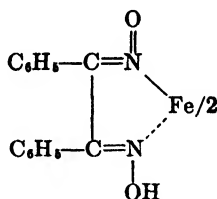
Ferrous benzildioxime[13]
water-insoluble
violet
stable
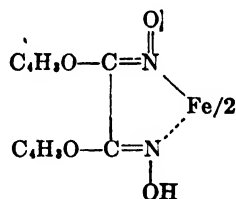
Ferrous furildioxime[14]
water-insoluble
blue
stable

Furthermore, since all aliphatic dioximes form soluble, red ferrous salts, it is apparent that the introduction of aromatic radicals not only exerts a distinct weighting effect, but also affects the structure of the ferrous salts and their color. It should be noted that this influence appears only among the ferrous dioxime compounds. In contrast, all of the inner complex salts of nickel and palladium with aliphatic and aromatic

[11] J. H. YOE, *J. Am. Chem. Soc.* **54**, 4139 (1932).

[12] L. TSCHUGAEFF and B. ORELKIN, *Z. anorg. allgem. Chem.* **89**, 401 (1914); see also Chapter VI.

[13] F. W. ATACK, *Analyst* **53**, 620 (1914).

[14] A. SOULE, *J. Am. Chem. Soc.* **47**, 981 (1925).

dioximes are insoluble in water.   Furthermore, all the nickel salts are red or orange, and all the palladium salts are yellow (compare Chapter VI).

The following summary, taken from unpublished studies with P. Krumholz, presents a comparison of the sensitivities of the tests for Ni^{++} and Fe^{++} ions by means of such dioximes as form insoluble nickel salts and soluble ferrous salts: The identification limits of the nickel tests were determined by impregnating paper (Schleicher and Schüll, No. 601) with $M/20$ alcoholic solutions of the oximes, drying, and then treating the paper with a drop of a neutral nickel solution and exposing to ammonia vapors.   α-Benzildioxime was used in hot saturated alcoholic solution. The iron tests were made, on a spot plate, by treating 2 drops of $N/10$ $FeSO_4$, acidified with sulfuric acid, with a drop of $M/20$ reagent solution and then with a drop of 2 N ammonia.

H—C(:NOH)—C(:NOH)—H.................. 8.0γNi.....0.2γFe
CH₃—C(:NOH)—C(:NOH)—H............... 4.0γNi.... 0.1γFe
CH₃—C(:NOH)—C(:NOH)—CH₃. .. .. 0.03γNi... 0.1γFe
C₆H₅—C(:NOH)—C(:NOH)—C₆H₅...... ...... 0:03γNi ..

These data show that among aliphatic dioximes, a marked weighting effect occurs only among the insoluble nickel salts and not among the soluble ferrous salts.   It should be noted that the introduction of C_6H_5 groups into the dioxime molecule does not further increase the sensitivity toward nickel ions.

The sensitivity determinations by Krumholz and Watzek[15] on the salts of the complex iodobismuthic acid with homologous heterocyclic bases furnish an additional example as shown by Table XX.   The sensitivity was determined by treating 2 drops of acid $BiCl_3$ solution, on a spot plate, with a drop each of 0.1 N alcoholic solution of the base and of 1 N KI solution.   The result of the reaction (orange-red precipitate) was compared then with the result of a control containing no base.

The sensitivity in the reaction between Bi^{+++}, I^-, and the homologous bases clearly increases considerably with increasing molecular weight of the base.   Obviously, the sensitivity of the reaction can be used as a measure of the solubility only so long as the visibility limit of the reaction has not been reached; any lowering of the solubility beyond this point is no longer apparent in the sensitivity data.
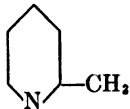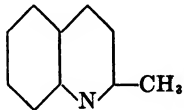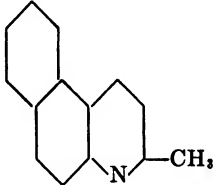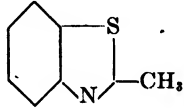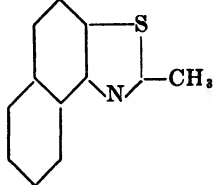
The dependence of the reaction sensitivity on the molecular weight of the base is quite evident also from a comparison of the sensitivity of the test for bismuth using different non-homologous heterocyclic bases. This is shown in Table XXI.

The sensitivity of the tests with the heterocyclic bases included in

[15] P. KRUMHOLZ and H. WATZEK, *Mikrochemie* **19**, 55 (1935).

Tables XX and XXI is considerably increased if the reagents are converted into quarternary compounds. For instance, it is raised about 50 times in the case of picoline. This effect is not to be regarded as due solely to weighting; it results also from an alteration in the structure of
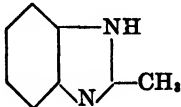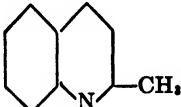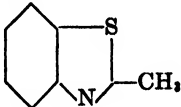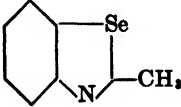
TABLE XX

Base	Formula	Molecular weight	Concentration limit in	
			0.25 N HCl	1 N HCl
α-Picoline		93	1:3,000	
Quinaldine..		143	1:75,000	1:30,000
β-Naphthoquinaldine.....		193	1:500,000	1:500,000
2-Methylbenzothiazole....		149	1:75,000	1:40,000
2-Methyl-α(β)-naphthothi-azole.		199	1:500,000	1:500,000

the molecule. It should be noted that the total weight of the salts formed is not increased to any considerable extent by the weighting of the organic components. For example, the difference in the molecular weights of the picoline and the quinaldine salts is only 7%, whereas the sensitivity of the reaction is increased about 25 fold. Obviously, the

solubility is not determined by the total weight of the salt, but primarily by the weight and the volume of the organic components.

TABLE XXI

Base	Formula	Molecular weight	Concentration limit in	
			0.25 N HCl	1 N HCl
2-Methylbenzimidazole...		132	1:10,000	1:5,000
Quinaldine..............		143	1:75,000	1:30,000
2-Methylbenzthiazole.....		149	1:75,000	1:40,000
2-Methylbenzselenazole...		196	1:300,000	1:150,000

An analogous effect has been observed by P. and E. Krumholz[16] in the formation of the double salts of zinc thiocyanate with heterocyclic styryl bases of the general formula:
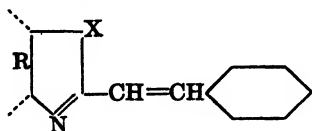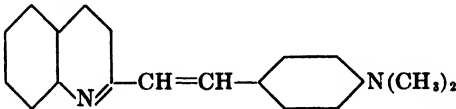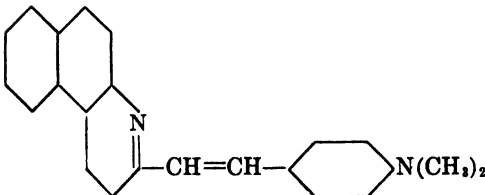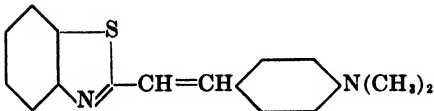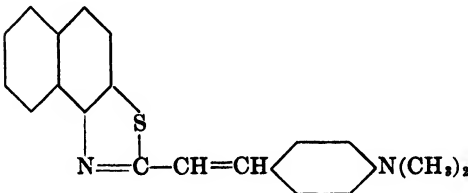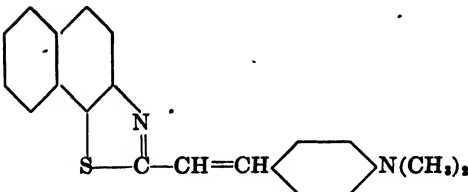
X = —CH=CH—, O, S, Se, N(CH₃)₂
R = C₄H₄, C₈H₆, etc.

Here again, as Table XXII shows, an increase in the molecular weight of the base results in an extraordinary rise in the sensitivity.

The sensitivity was determined by treating 1 ml. of 0.2 N HCl solution containing Zn++ with 0.1% alcoholic solution of the styryl base, and then with 3 drops of 20% potassium thiocyanate solution. The resulting color was compared with that obtained in a blank containing no zinc. The color in the blank is yellow to orange, that of the test portion containing zinc is reddish to violet.

16 P. KRUMHOLZ and E. KRUMHOLZ, *Mikrochemie* 19, 47 (1935).

TABLE XXII

Reagent	Drops of reagent	Concentration limit
(quinoline ring)—$CH=CH$—(benzene ring)—$N(CH_3)_2$	5	1:10,000
(isoquinoline/naphthalene ring) N —$CH=CH$—(benzene ring)—$N(CH_3)_2$	5	1:10,000,000
(benzothiazole ring S, N)—$CH=CH$—(benzene ring)—$N(CH_3)_2$	5	1:50,000
(ring) $N=C$—S—$CH=CH$—(benzene ring)—$N(CH_3)_2$	1	1:10,000,000
(ring) S—C—$CH=CH$—(benzene ring)—$N(CH_3)_2$	1	1:10,000,000

The following observations[17] indicate the effect on the solubility of certain salts in water and organic solvents when the molecule is weighted. The sodium salt of pyruvic acid, $CH_3 \cdot CO \cdot COOH$, in aqueous solution, forms no precipitates with iron or copper salts. If, however, solutions of its hydrazones of the general formula

$$\begin{array}{c} R_1 \\ {\large>} N-N=C \\ R_2 \end{array} \begin{array}{c} CH_3 \\ \\ COOH \end{array}$$
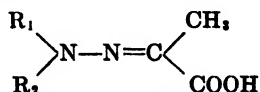
[17] Taken from unpublished studies of F. FEIGL with H. ZENTNER and E. KANNER. Compare Dissertations, Vienna, 1924.

are used, in which R_1 and R_2 represent the following groups

	I	II	III	IV	V
R_1............................	H	CH_3	H	H	H
R_2............................	C_6H_5	C_6H_5	$C_{10}H_7$	$C_6H_4(NO_2)$	$C_6H_2(NO_2)_3$

the findings are:

I forms no insoluble copper salt, but with iron salts gives a precipitate whose composition is not uniform.

II forms a definite copper salt and an indefinite iron salt.

III, IV, V form definite copper and iron salts.

Accordingly, the groups contained in the hydrazones I to V exhibit a weighting effect. Furthermore, all of these copper and iron salts are insoluble in organic solvents, such as ether, chloroform, or acetone.

The introduction of the radicals

	I	II	III	IV	V	VI
R_1....	H	H	H	H	C_6H_5	C_6H_5
R_2....	$C_6H_4Br(p)$	$C_6H_4I(p)$	$C_6H_3Br_2(2,4)$	$C_6H_4COC_6H_5(p)$	$CH(C_6H_5)_2$	$CH_2C_6H_5$

results in not only the formation of definite insoluble copper and iron salts, but also leads to a considerable solubility of these salts in the foregoing organic solvents. It is remarkable that this solubility is not due solely to any solubility of the organic components, but is acquired only because of the salt formation. This is also shown by the slight solubility of p-benzoylphenylhydrazonepyruvic acid (I) in acetone, of diphenylhydrazonepyruvic acid (II) in ether, and of p-iodophenylhydrazonepyruvic acid (III) in chloroform, while their copper and iron salts dissolve very easily in these media.

$$H_3C-\overset{\underset{\displaystyle N}{\|}}{C}-COOH$$
$$NH-C_6H_4COC_6H_5$$
(I)

$$H_3C-\overset{\underset{\displaystyle N}{\|}}{C}-COOH$$
$$N\underset{C_6H_5}{\overset{C_6H_5}{<}}$$
(II)
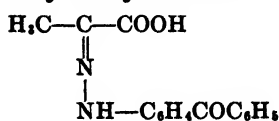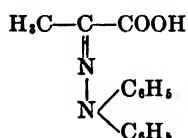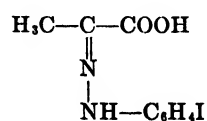
$$H_3C-\overset{\underset{\displaystyle N}{\|}}{C}-COOH$$
$$NH-C_6H_4I$$
(III)

These examples demonstrate the remarkable effect that groups which lower the solubility in water can raise the solubility of heavy metal salts in organic solvents.

A further instance is provided by the hydrazones of the α-ketonic acids, where a group action is clearly evident. The hippurylhydrazone of pyruvic acid

$$C_6H_5CONHCH_2\!\!-\!\!CO\!\!-\!\!NH\!\!-\!\!N\!\!=\!\!C\!\!<\!\!{}^{CH_3}_{COOH}$$
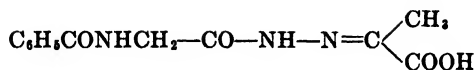
though of higher molecular weight and containing more atoms than many of the foregoing compounds, is nevertheless incapable of forming insoluble copper and iron salts. In all likelihood, the water-solubility of these salts is due to the presence, in the hippuryl radical, of a hydration center, namely the NH group, which exhibits a similar action in other cases.

Numerous examples in this and the preceding chapter show that the water-solubility of organic compounds, and of salts of organic acids and bases, can be ascribed to the presence of hydratable atoms and atomic groups. These groups serve as the vehicle or promoter for the solubilization of the entire molecule. It is obvious that this function of a hydratable group cannot be unlimited; it will tolerate weighting within certain bounds only. Accordingly, a marked weighting effect can be considered as the tangible expression of an overloading of that part of the molecule to which the hydratable group is bound. This conception of a weighting effect is plausible in many cases. If it is assumed that the solubility of a compound requires the presence of a hydration center, then the elimination of this center, or every diminution of its ability to add water, must result in the disappearance, or at least a decrease, of the solubility in water. A weighting effect may thus also be expected if a hydration center is "hemmed in" by the introduction of one or more groups into the molecule. It is clear that even atomic groups of small weight may then have distinct effects in lowering the solubility. Excellent examples of weighting effects due to the removal of a hydration center can be drawn from the studies by Schaeffer.[18] He investigated the barium and benzidine salts of 1-naphthylhydrazine-5-sulfonic acid (I) and 1-hydrazine-5-naphthoic acid (III). These salts, which are quite soluble in hot water, react almost immediately with aliphatic and aromatic aldehydes (but not with monoketones) to produce the corresponding hydrazones, (II) and (IV), without change in other parts of the molecule. The products are not soluble in water; some of them are highly colored.

(I)   (II)
Water-soluble   Water-insoluble
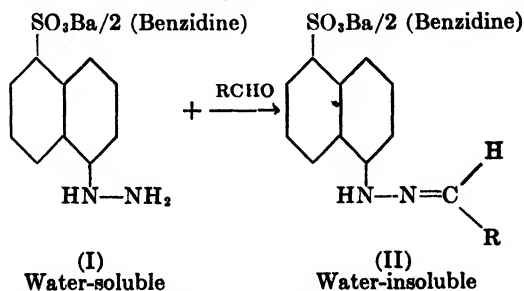
[18] A. SCHAEFFER, Inaugural Dissertation, Munich, 1906.

CO_2 Ba/2 (Benzidine) CO_2 Ba/2 (Benzidine)

$$\text{(ring system)} \;\; HN\text{—}NH_2 \quad + \quad \xrightarrow{\text{RCHO}} \quad \text{(ring system)} \;\; HN\text{—}N\text{=}C\underset{R}{\overset{H}{\diagdown}}$$

(III)   (IV)
Water-soluble   Water-insoluble
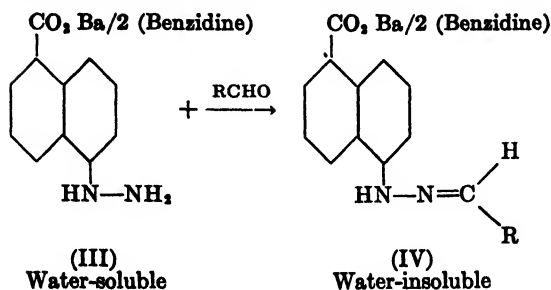
A comparison of these compounds and their respective products shows clearly that the ability to add water was removed from the hydratable hydrazine group after formation of its hydrazone. Thus, this group loses its function as the vehicle of the water-solubility of the barium or benzidine salts of these particular acids. It is in agreement with the foregoing that even the lowest aldehyde (formaldehyde), and also the polyatomic aliphatic and aromatic aldehydes, act in the same way in these condensations, and confer insolubility on the barium and benzidine salts. The various resulting hydrazones differ only in color. It may be safely predicted that hydrazone-sulfonic acids of this type will be precipitating reagents for Ba^{++} ions, and that they will form water-insoluble colored barium salts.

The introduction of certain atoms and atomic groups into organic compounds has been considered thus far with regard to the accompanying weighting effect, *i.e.*, with reference to an influence exerted by the increase of the molecular weight on the solubility in water and organic solvents. However, it must be remembered that the introduction of atoms and atomic groups into an organic compound may also increase the volume of the molecule. Consequently, the possibility of a size effect, in addition to a weighting effect, must be taken into account. Among organic compounds that function as reagents because they contain certain reactive groups, additional weighting and size effects can be of great analytical significance through their influence on the solubility of the reagent, on its ability to form salts, and on the solubility characteristics of the reaction products. In many cases, it is difficult to decide whether atomic groups that have been introduced into the molecule of the organic compound exert a weighting or a size effect. The tendency always is to assume weighting effects, because numerical values of an increase in weight are obvious. However, there are instances of group actions that permit a clear differentiation between weighting effect and size effect. The studies of Willink and Wibaut[19] give the following comparative picture of the behavior toward ferrous salts of α,α'-dipyridyl (I), 6,6'-

[19] H. TJWEENK WILLINK, JR., and J. WIBAUT, *Rec. trav. chim.* **54**, 275 (1935).

dimethyl-2,2'-dipyridyl (II), 6,6'-diamino-2,2'-dipyridyl (III), and α,α'-phenanthroline (IV):
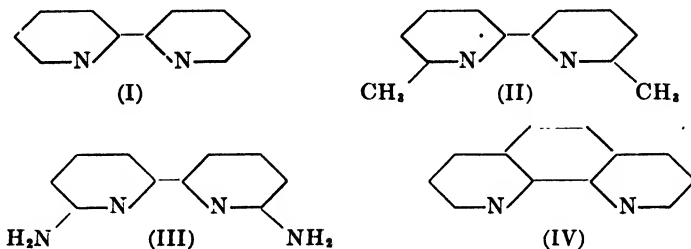
| Molecular weight | 156.1 | 184.1 | 186.1 | 180.1 |
| Ferrous reaction | Positive | Negative | Negative | Positive |

The term "ferrous reaction" signifies the formation of ammine salts or red complex ferrous ammine ions in solutions containing mineral acids (compare Chapter V). This weighting of the parent compound (I) leads to derivatives (II) and (III), whose molecular weights do not differ significantly. Nevertheless, the reactivity toward ferrous ions has been lost in them, while it has been retained in (IV). Clearly, there is no weighting effect here, but rather an effect which shows itself in influencing the salt-forming ability of the dipyridyl group contained in (I) to (IV). This group, as the complex ion $[Fe(\alpha,\alpha'\text{-dip})_3]^{++}$ shows, forms salts through its coordination on the iron atom, with production of hexammine ions. Accordingly, three complete molecules of the base must be coordinated on the iron atom. An enlargement of the molecular volume of the base may lead to a spatial condition in which there is not sufficient room for the stable placement of three molecules of the base. Under such circumstances, there can be no addition of these molecules, even though coordinative nitrogen atoms are present. The inactivity of ferrous ions towards (II) and (III) can be explained plausibly by assuming that the CH_3 and NH_2 groups in these compounds sufficiently enlarge the volume of the molecule of the base so that the salt-forming ability, through coordination of the dipyridyl group, no longer functions.

It is natural to suppose that size effects will be particularly effective when complex compounds are to be formed. The reason is that every coordination involves not only an activity of binding forces, but also, at the same time, a space requirement. However, both the volume of the coordinated molecule and the volume of the atom on which coordination occurs are significant in the production of size effects. These considerations were followed by Merritt and Walker[20] in explaining the divergent analytical behavior of the homologous compounds, 8-hydroxyquinoline

[20] L. L. MERRITT and I. K. WALKER, *Ind. Eng. Chem., Anal. Ed.* **16**, 387 (1944).

(I) and 8-hydroxyquinaldine (II):
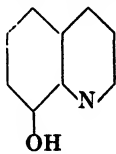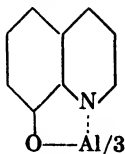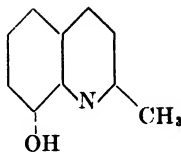
(I) I(a) (II)

An inner complex aluminum salt (Ia) is formed by (I), but not by (II). Furthermore, a quantitative precipitation of an inner complex ferric salt is obtained with (II), but only from solutions which are much less acidic than when (I) is used as the precipitant. In this instance the introduction of a methyl group alters the ability to form a salt and increases the selective activity. Merritt and Walker are correct in their statement that, if the size of the complex-forming molecule is a determining factor, the larger molecule might be expected not to react with the smaller ion, because of the difficulty in grouping three large molecules around the small ion. If the complex is formed, it may be less stable. This is well demonstrated by the behavior of (I) and (II) toward aluminum and iron ions.

Size effects play a part in the activity of atomic groups already present in organic compounds or that are subsequently introduced into them. This is in agreement with the experience that slightly soluble salts often result from the union of polyatomic ions or molecules. The precipitability of polyatomic organic bases by acids with large anions has been known for a long time. It is the basis, for instance, of a general test for alkaloids in acid solution by precipitation with phosphomolybdic acid, phosphotungstic acid, polyiodides, *etc.* A quasi-inorganic counterpart was cited on p. 323, namely, the precipitability of the complex $[Fe(\alpha,\alpha'\text{-dip})_3]^{++}$ ions by alkaloid reagents. The objection that the precipitability is not due to the increased ionic volume resulting from the addition of the base but rather to the consequent greater weight can be met by citing a more convincing illustration of a size effect, namely the comparison of the behavior of $[Cu(H_2O)_4]^{++}$ and $[Cu(NH_3)_4]^{++}$. Although they are practically equal with respect to weight, only $[Cu(NH_3)_4]^{++}$ ions are precipitated by I^- or $[HgI_4]^{--}$ ions. Since an addition of molecules of organic bases has the same effect as ammonia, it is probable that a size effect is always involved in such additions. This fact becomes evident in the precipitability of the resulting complex ions. Spacu[21] showed that the addition of

[21] G. SPACU, *Z. anal. Chem.* **77**, 334, 340 (1929); **78**, 224, 329 (1929); **79**, 196 (1929); **92**, 247 (1938).

ethylenediamine or pyridine to metal ions, and the precipitability of the resulting complex ions with complex anions, can be used as the basis of very accurate gravimetric methods for determining copper, cadmium, and mercury, since the metal content of the precipitates is particularly low.

It is worth noting that a size effect sometimes can have more importance than a weighting effect in producing insolubility, or in lowering the solubility, in homologous or analogous salts. A good example of this is given by comparing the behavior of the dibasic rhodizonic acid, $C_6O_4(OH)_2$, with ammonia, methylamine, ethylenediamine, and aniline.[22] If a saturated (approx. 0.2%) solution of sodium rhodizonate is treated with approximately 0.1 N solutions of the hydrochlorides of these bases, violet crystalline precipitates are formed only with ethylenediamine and aniline. Ammonium chloride and methylamine hydrochloride have no action. However, the aniline salt of rhodizonic acid is more soluble than the ethylenediamine salt, even though 1 mole of acid unites with 2 moles of aniline, and with only 1 mole of ethylenediamine. This corresponds to a weight relation of 186:60. The extent of the solubility differences, despite the weighting effect of the C_6H_5 group of the aniline, is shown by the fact that, under like conditions, a spot reaction on filter paper will reveal (formation of a violet fleck) 0.23γ of ethylenediamine as opposed to 500γ of aniline. The strikingly low solubility of ethylenediamine rhodizonate is undoubtedly due, as shown by the formula of this salt, to a ring closure effected by principal valence binding, which can be regarded as filling space and; therefore, as a size effect. The following comparison of the solubility of ethylenediamine rhodizonate (I) with that of methylamine rhodizonate (II), of practically the same weight, and with that of the much heavier aniline rhodizonate (III), reveals how dominant the influence of a ring closure and, therefore, of a size effect, can be:
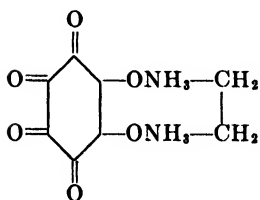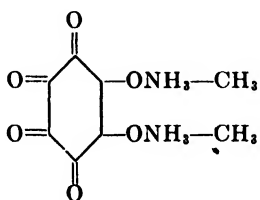
(I)	(II)	(III)
230	232	404
Insoluble	Soluble	Medium solubility
Size effect	Neither size nor weighting effect	Weighting effect
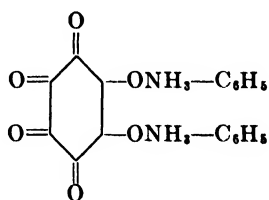
[22] F. FEIGL and H. E. FEIGL, unpublished studies.

TABLE XXIII

Parent acid	Solubility in water	Alkaline earth salt	Solubility
H_2SO_4	Miscible	$(SO_2)\!\!<^O_O\!\!>E$	Insoluble in water and acids
$C_6H_5SO_2H$	Limited solubility	$C_6H_5—(SO_2)—O\,\dfrac{E}{2}$	Soluble in water
H_3PO_4	Miscible	$(PO)\!\!<^O_O\!\!>O—E(\frac{3}{2})$	Insoluble in water
$C_6H_5(PO)(OH)_2$	Soluble	$C_6H_5—(PO)\!\!<^O_O\!\!>E$	Soluble in water
$(C_6H_5)_2(PO)(OH)$	Insoluble	$\begin{matrix}C_6H_5\\ \diagdown\\ \quad(PO)—O\,\dfrac{E}{2}\\ \diagup\\ C_6H_5\end{matrix}$	Soluble in water
H_3AsO_4	Soluble	$(AsO)\!\!<^O_O\!\!>O—E(\frac{3}{2})$	Insoluble in water
$C_6H_5(AsO)(OH)_2$	Slightly soluble at room temperature	$C_6H_5—(AsO)\!\!<^O_O\!\!>E$	Insoluble in water
$(C_6H_5)_2(AsO)(OH)$ ...	Difficultly soluble at room temperature	$\begin{matrix}C_6H_5\\ \diagdown\\ \quad(AsO)—O\,\dfrac{E}{2}\\ \diagup\\ C_6H_5\end{matrix}$	Soluble in water
H_3BO_3	Soluble	$B\!\!<^O_O\!\!>O—E(\frac{3}{2})$	Insoluble in water
$(C_6H_5)B(OH)_2$	Soluble in hot	$C_6H_5—B\!\!<^O_O\!\!>E$	Insoluble in water
$(C_6H_5)_2B(OH)$	Insoluble	$\begin{matrix}C_6H_5\\ \diagdown\\ \quad B—O\,\dfrac{E}{2}\\ \diagup\\ C_6H_5\end{matrix}$	Soluble in water
H_3AsO_4	Soluble	$(AsO)\!\!<^O_O\!\!>O—Zr(\frac{3}{4})$	Insoluble in water and acids
$C_6H_5(AsO)(OH)_2$	Slightly soluble at room temperature	$C_6H_5—(AsO)\!\!<^O_O\!\!>\dfrac{Zr}{2}$	Insoluble in water and acids

The slight solubility of ethylenediamine rhodizonate makes possible a selective test for ethylenediamine.[22a]

If, as shown by the case of ethylenediamine rhodizonate, a ring closure is regarded as a size effect that can have greater significance for the slight solubility of a salt than a weighting effect, then the striking contrast in the solubilities of salts of phenylated mineral acids can be plausibly explained. Benzenesulfonic acid is a sulfuric acid which is weighted by a C_6H_5 group, and the weighting effect reveals itself in the fact that this acid is less water-soluble than sulfuric acid. Consequently, in considering a weighting effect which also is reflected in the salts, it might be expected that the alkaline earth salts of benzenesulfonic acid would be less water-soluble than the corresponding sulfates. However, the exact opposite is the case; the alkaline earth salts of benzenesulfonic acid (and of other alkylated sulfonic acids) are quite soluble in water. Perhaps this can be ascribed to the fact that, in contrast to sulfuric acid, there is no possibility of a ring closure when the salt of the monobasic benzenesulfonic acid is formed. This assumption is confirmed by a comparison of the solubilities of the alkaline earth salts of phosphoric, arsenic, and boric acid, with the solubilities of the corresponding salts of mono- and diphenylated phosphoric, arsenic, and boric acid. The data are given in Table XXIII in which E = Ba, Ca, or Sr.

A comparison of these data for the solubility in water of sulfuric, arsenic, phosphoric, and boric acids, and of their phenyl derivatives, reveals plainly the weighting effects of the C_6H_5 groups. The presence of two acidic OH groups in the monophenylated arsenic, boric, and phosphoric acids, provides the possibility of a ring closure when the salts of divalent metals are formed. Therefore, in analogy to the normal phosphates, arsenates, and borates, the alkaline earth salts retain their slight solubility in water. There is no possibility of a ring closure in the diphenylated and consequently monobasic acids. Accordingly, these acids, which are not soluble in water, behave entirely like the monobasic benzenesulfonic acid, despite their being weighted by two C_6H_5 groups; the alkaline earth salts are water-soluble. In harmony with this finding, phenylarsinic acid retains the property of arsenic acid of forming a zirconium salt that is not soluble in water or acids.[23] This fact was

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[22a] No gravimetric method of determining ethylenediamine has been worked out as yet. It appears that in addition to salt formation with rhodizonic acid, condensation reactions with the CO groups of this acid may intervene.

[23] In conformity with the regularities contained in the preceding table, which probably apply to all alkylated mineral acids, diphenylarsinic acid,

$$(C_6H_5)_2:(AsO)\cdot(OH)$$
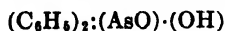
in contrast to phenylarsinic acid, cannot be expected to act as a precipitating agent

observed by Rice, Fogg, and James[24] and forms the basis of their procedure for separating zirconium from other elements, and for its gravimetric determination. The sensitivity and the selectivity of the precipitation of zirconium by phenylarsinic acid is considerably greater than that by arsenic acid. This characteristic can be viewed as visible evidence of a weighting effect of the C_6H_5 group.

Weighting and size effects are distinctly evident in the behavior of solutions of ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) and its anionic inner complex salts toward ferrous α,α'-dipyridyl salts.[25] As noted in Chapter VI, $[Fe(\alpha,\alpha'\text{-dip})_3]^{++}$ ions serve as general precipitants for voluminous, and especially for complex, anions. They combine with the latter to form water-insoluble, red $[Fe(\alpha,\alpha'\text{-dip})_3]$ salts. Ferron is likewise precipitable with $[Fe(\alpha,\alpha'\text{-dip})_3]SO_4$, but only from solutions that contain more than 0.25% of the sulfonic acid. The red precipitate is a salt of ferron and corresponds to (II). Ferron is only slightly soluble in water, and a saturated solution (0.2%) does not react with $[Fe(\alpha,\alpha'\text{-dip})_3]SO_4$. Consequently, solutions of sufficient concentration to give a precipitate with ferrous dipyridyl salts can be prepared only from the quite water-soluble alkali salts of ferron. However, if a saturated solution of ferron is treated with ferric chloride (blue color, see page 187), or if lead or thorium nitrate, *etc.*, is added to an ammoniacal solution of ferron, a red precipitate is thrown down immediately by $[Fe(\alpha,\alpha'\text{-dip})_3]$-$SO_4$. The following explanation is offered. The hydrogen of the phenolic OH group of ferron can be replaced by one equivalent of iron, lead, thorium, *etc.*, and soluble salts of ferron with inner complex anions are formed. In such cases the SO_3H group, that can be salified with $\frac{1}{2}[Fe(\alpha,\alpha'\text{-dip})_3]$, remains unaltered, or its ammonium salt is formed in the ammoniacal solution. Only the anionic portion of the sulfonic acid is altered. This part of the compound is weighted by the inner complex installation of a metal atom, and its volume is expanded. The result is the precipitability of quantities of ferron that, without weighting and expansion, do not react with ferrous dipyridyl sulfate. The $[Fe(\alpha,\alpha'\text{-dip})_3]$ salts of the complex acids formed from ferron correspond to (III):

for zirconium, despite the extra weighting by a second C_6H_5 group. There is no experimental proof of this as yet.

[24] A. Rice, H. Fogg and C. James, *J. Am. Chem. Soc.* **48**, 895 (1926).

[25] F. Feigl and K. Soria, unpublished studies.

SO₃H
SO_3H

$SO_3[\frac{1}{2}Fe(\alpha,\alpha'\text{-dip})_3]$

$SO_3[\frac{1}{2}Fe(\alpha,\alpha'\text{-dip})_3]$

I HO

I HO

I $\text{HO}—\text{Me}^{\cdot}$

(1)
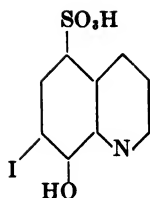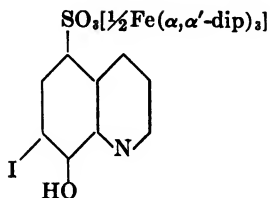
(II)
Soluble if ferron = 0.2%
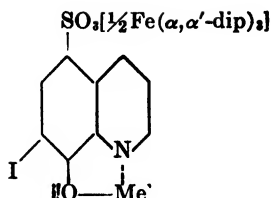
(III)
Insoluble if ferron = 0.2%
(Me = $\frac{1}{3}$Fe, $\frac{1}{2}$Pb, $\frac{1}{4}$Th, *etc.*)

This effect of the transformation of ferron into a complex acid (or its anion) that can be precipitated by $[Fe(\alpha,\alpha'\text{-dip})_3]^{++}$ ions is easily demonstrated. It is merely necessary to mix a saturated solution of ferron with a solution of $[Fe(\alpha,\alpha'\text{-dip})_3]SO_4$ and then add ferric chloride to the red solution. Alternatively, an ammoniacal solution of the reagent can be treated with $Pb(NO_3)_2$, $Zr(NO_3)_4$, *etc.* Inner complex anions are formed at once, and there is immediate precipitation of the red ferrous dipyridyl salt. This effect will reveal quantities of iron, lead, thorium, *etc.*, that are too small to produce visible precipitates of the hydrous oxides. As in many other cases cited in this section, it cannot be stated whether the effect of an equivalent of metal introduced in the molecule of ferron should be regarded as a weighting or a size effect. Probably both are involved.

★ ★ ★ ★

The discussions in the preceding four chapters show that the activity of certain groups is undoubtedly responsible for the specific and selective action of organic reagents, and for the solubility relationships that are so important in analytical procedures. These facts are vital to the understanding of the action of organic reagents, and for investigations directed toward the discovery of new reagents or the improvement of those now in use. · Consequently, a consideration of all observations of group actions is essential, because the knowledge and experiences concerning the specificity and selectivity of reactions and tests will then rest on a broader and more stable foundation.

CHAPTER X

Surface Effects in Analytical Chemistry

Many analytical procedures consist of direct chemical actions on solid materials or of the production of precipitates. Consequently, the analyst is forced to consider such properties and modifications of properties of solids as are related to the general attribute of solids, namely, their free surface. A surface *per se* has no direct chemical and physical activity; it is merely the seat of energy effects. Therefore, it need only be considered as a capacity factor, and accordingly a given quantity of a material may possibly exhibit appreciable modifications in properties as its surface increases. Solid structures with highly developed surfaces may be the object of analytical examinations, or they may be introduced or formed during the course of such chemical operations. Sometimes the products of chemical changes have highly developed surfaces and the varying stability of this dispersity can be responsible for a particular reaction picture. Finally, the mere presence of materials with highly developed surfaces in the *milieu* of chemical reactions or solutions may have an important influence; even though these materials do not appear as participants in the stoichiometrically defined reaction. It is thus apparent that the formation and activity of surface-rich materials cannot be irrelevant factors in any consideration of the problems of specificity, selectivity, and sensitivity of tests. Such surface effects as have analytical bearings will be discussed in this chapter and also, in part, in Chapter XI.

COLOR, SOLUBILITY, AND SUSPENDIBILITY OF SOLIDS AS A FUNCTION OF PARTICLE SIZE

The significance of free surface is perhaps most strikingly evidenced by the fact that the solubility of a solid, a value often regarded as a characteristic numerical value for a given material, is, in fact, not a constant. Solids give solubility values that are practically identical and reproducible only when the determinations are made with samples whose particles have a diameter greater than $10-20\mu$ ($1\mu = 0.001$ mm.). Below this value, there is a distinct increase in solubility with progressive diminution in the size of the particles. In other words, the material becomes more soluble with increase in its specific surface. The latter is defined as the surface per unit weight. P. Curie[1] seems to have been the first to point out that, if a number of crystals of different sizes are in

[1] P. CURIE, *Bull. soc. franç. minéral* **8**, 145 (1885).

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contact with a solution which is saturated with respect to the larger crystals, the smaller crystals may dissolve, and the additional dissolved material will then deposit on the larger crystals. The result is a decrease in the total surface of the solid, and consequently the total surface energy between the solid and liquid is lessened. Improvement in the filtrability of freshly precipitated materials, especially crystalline precipitates, by allowing them to stand in contact with the mother liquor, usually at moderately elevated temperatures, is a familiar analytical practice. This expedient owes its efficacy to the production of coarser grained particles, which are also more uniform in size. Although other effects are involved, this result is partly due to the growth of the larger particles at the expense of the smaller more soluble ones, which eventually disappear.[2] In his classic studies with mercuric oxide and lead iodide, Wilhelm Ostwald[3] showed that the smaller particles of these compounds are definitely more soluble than the coarser ones. Dundon,[4] using more modern methods, gave a striking demonstration of the relationship between particle size and solubility. He showed that the addition of very finely ground gypsum to a saturated solution of $CaSO_4$, or of heavy spar to a saturated $BaSO_4$ solution, brought about an increase in the conductivity of the solution. It rose to a maximum and then slowly declined to the original value. This conductivity picture clearly demonstrates three points: (a) the greater solubility of the smaller particles; (b) the condition known as supersaturation; (c) the instability of the supersaturation in the presence of coarser particles of the solute. The definite effect of its particle size on the solubility of a solid is also illustrated by the following findings. Hulett[5] observed no change in solubility of $CaSO_4$ crystals larger than 2μ, but decreasing the size to 0.3μ raised the solubility about 20% at 25°C. Jaeger[6] found that dehydrated Al_2O_3 or ZrO_2, which ordinarily do not dissolve in hydrochloric acid, are

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[2] The increase in the grain-size of a precipitate at the expense of the smaller, more soluble particles is known as Ostwald ripening. It was long believed that this was the decisive effect in the aging of difficultly soluble precipitates at room temperature. However, Kolthoff and his coworkers, in a series of experimental studies with analytical precipitates containing lead, silver, and barium, have shown that other factors are of prime importance. The change in filtrability on digestion must be attributed to the perfection by recrystallization of the very imperfect crystals that come down initially, and to the collection of smaller particles into larger clumps, followed by the cementing together of the small particles into larger aggregates that are retained by the filter. For details and references to the literature consult I. M. KOLTHOFF and E. B. SANDELL, Textbook of Quantitative Inorganic Analysis, New York, 1943, p. 105.

[3] WI. OSTWALD, Z. physik. Chem. **34,** 495 (1900).

[4] M. L. DUNDON, J. Am. Chem. Soc. **45,** 2658 (1923).

[5] G. A. HULETT, Z. physik. Chem. **37,** 385 (1901).

[6] F. M. JAEGER, Z. anorg. allgem. Chem. **101,** 385 (1917).

rendered somewhat soluble if the particle size is reduced to less than 2.5μ. The dependence of the solubility of solids on their particle size is of considerable importance when solids are produced from solutions as a result of chemical reactions. If no solid phase is present, some degree of supersaturation invariably precedes the precipitation. This inevitable condition, which is due to the higher solubility of the finer particles, cannot persist in the presence of the solid phase, and the supersaturation breaks down at a rate that varies from case to case, depending on the temperature, stirring, presence of other solutes, *etc.* (see Chapter XI).

Other physical properties, as well as solubility, may be functions of the particle size. Three of these surface-dependent properties, which have analytical importance, are: rate of solution, color, and suspendibility.

Finer particles of a solid dissolve in water more rapidly than coarser ones.[7] At a given temperature, the saturation concentration is therefore reached sooner the more finely divided the particles. The rate of solution, frequently called dissolution, in chemically active solvents is likewise greater if finer particles are presented to the solvent. Consequently, in analytical procedures, solids are usually pulverized before they are subjected to solution or fusion processes.[8] A preliminary grinding is always advantageous in identification procedures in which the reagents are applied directly to the solid sample, and is particularly recommended if the tests are not very sensitive. This is in line with the idea that reactions of solids with dissolved reagents always involve those

[7] The rate $\frac{dc}{dt}$ at which a solid goes into solution at a given temperature, depends not only on the free surface (*o*) but also on the differences between the saturation concentration (c_s) and the concentration (*c*) prevailing at the time (*t*). This rate can be represented by the equation $\frac{dc}{dt} = k.o.(c_s - c)$, in which *k* is an individual proportionality factor. This equation, which has been found to hold in many instances, is based on the fact that a very thin film of saturated solution rapidly forms on the surface of the solid. The dissolved molecules then diffuse out of this layer into the body of the solvent. Consequently, the rate of solution of a solid, at a given temperature, is determined both by the extent of the free surface of the solid and by the diffusion velocity of the dissolved portions. These considerations also apply to the reaction velocity of changes in heterogeneous systems (solid-liquid). In such cases, the rate at which the reaction proceeds depends on the diffusion velocity of a soluble reaction product. L. BRUNNER [*Z. physik. Chem.* **47**, 56 (1904)] states that the depth of this diffusing layer may reach 20 to 50μ.

[8] It should be noted that the reduction of materials to very fine powders may also result in chemical effects. Instances are oxidation of sulfides, sulfites, ferrocyanides, *etc.*, loss or absorption of moisture, and sometimes chemical reactions between the solid constituents of a mixture. This is a result of the fact that increase in the free surface of solids is accompanied by an enhancement of their analytically significant reactivity toward gaseous reactants or toward solids that are in direct contact with the material being pulverized. (Compare Chapter XI.)

portions of the solid which have gone into solution and which are then replenished after they have been consumed. The higher rate of solution and the greater actual solubility of smaller particles make it possible to use almost insoluble compounds as reagents, provided care is taken to disperse them sufficiently. Advantage is taken of this fact in spot test papers. These often are impregnated with reagents that are practically insoluble, and yet they respond quickly because of the high state of division of the active material distributed throughout the capillaries of the paper.

The relation of the color of solids to their particle size is even more impressive than the corresponding dependence of the rate of solution, because the color differences can often be seen directly. It is common knowledge that the color of large crystals or compact fragments of minerals often differs markedly from that of the powdered material. Consequently, a streak plate is an essential aid in determinative mineralogy and in the qualitative examination of minerals. As its name indicates, this is a rough porcelain plate, on which streaks of the sample can be made in order to determine the powder-color of the mineral. Examples of the color differences between coarse and fine powders are: CdO—black and brown; Sb_2S_3—crimson and yellow; $K_3Fe(CN)_6$—red and yellow; $K_2Cr_2O_7$—orange and yellow. The color of As_2S_3 changes from yellow to red as the coarseness increases. Similarly, PbO goes from red to yellow. The X-ray lattices of these color varieties are sometimes different, showing that the difference in color is not always entirely due to a difference in the size of the particles. Large crystals of $CuSO_4 \cdot 5H_2O$ are blue, but on grinding all shades to almost white are obtained. The same is true of $KCr(SO_4)_2 \cdot 12H_2O$, which is violet in coarse crystals. The changes in color (lightening or sometimes actual shift of color) of the light reflected from the surfaces of the powder is due to the fact that the thickness of the layer which the light traverses before it is again reflected decreases with increasing diminution of size of the particles, i.e., with increasing surface.

Compact and finely divided metals exhibit particularly striking color differences. If solutions of salts of Ag, Pt, Pd, Pb, and Bi are reduced, the finely divided metal forms a deep black precipitate, whose color is in marked contrast to the silvery white appearance of compact specimens of these metals. The great analytical importance of particle size is shown in tests that involve such reductions to the metal. Their deep black color makes these deposits easy to see; consequently the sensitivity of such reactions is quite high. For example, the formation of crystalline black-brown BiOI is distinctly less perceptible than the precipitation of an equivalent quantity of black finely divided metallic bismuth. Other

precipitates also show color differences that can be attributed to differences in particle size. Thus, freshly precipitated Au(OH)$_3$ is light greenish yellow; on long standing it passes through red-yellow to an ochre-brown product. Thallous iodide on standing passes from yellow to a definite green. Mercuric oxide is egg-yellow if precipitated at room temperature; it turns red when heated, because the particles become larger.

The thorium salt of 8-hydroxyquinoline, if precipitated at room temperature, is lemon yellow and has the composition

$$Th(C_9H_6NO)_4 \cdot C_9H_7NO \cdot xH_2O$$
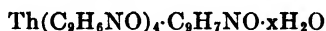
In contrast, the product obtained by precipitation at 80–90°C. is orangered. It doubtless contains less water than the yellow precipitate.

Differences in dispersion, due to varying the conditions of precipitation, are responsible for the production of either yellow or orange-red cadmium sulfide, or bright yellow to brown-yellow palladium dimethylglyoximate. Less striking, but nevertheless recognizable, differences in shade are frequently seen in other colored precipitates, and on comparing colored precipitates of the same compound that are moist, that have been aged under water, or that have been dried.[9]

As a rule, colored precipitates are darker the coarser the grain size, the shift in shade being generally toward red. A striking instance of such deepening toward red is found in nickel dimethylglyoximate. Everyone who has closely observed the precipitation of this compound from a warm solution knows that the addition of the reagent often produces at first a honey-yellow to orange solution. This color disappears in proportion

[9] In the latter case, namely, in the comparison of moist and dried products, there is, in addition to the color differences originating in the differing particle-sizes, an effect due to light refraction of the medium (air, water, or other liquid) that surrounds the particles. The smaller the difference in the light refraction in the colored material and in the enveloping medium, the more intense the color. Consequently, precipitates moistened with water usually appear darker than the dried material. However, the converse phenomenon occurs and can be observed when gelatinous precipitates are dried. For instance, precipitated moist Fe$_2$O$_3$·aq and Cr$_2$O$_3$·aq are brown and grey-green, respectively; when dried the products are deep brown and deep green to black. The reason is that the water which disappears in the drying is not replaced by air. Instead, the particles of the precipitate adhere more closely to each other, an effect that is tantamount to an increase in particle size. Accordingly, when these dark dried products are pulverized, they recover their lighter colors. If water is a constituent part of a precipitate, part of it may be lost on drying and any resulting color change is independent of the particle size. For example, light blue Ni(CN)$_2$·4H$_2$O loses water when dried and turns yellow. Nickel dicyandiamidine (see p. 207), which is yellow when combined with two molecules of water of crystallization, becomes flesh colored when dried. Cobalt salts provide many other pertinent examples.

to the production of the precipitate, whose particles are pink in the beginning and then change to the familiar scarlet. The yellow or red color of the preceding solution is due to nickel dimethylglyoximate, whose true or highly dispersed colloidal solution is not red but yellow. This fact is also shown by the yellow, not red, solutions invariably obtained when the dry salt is dissolved in chloroform, molten paraffine, warm oleic acid, *etc.* Other examples demonstrating the dependence of the color of an insoluble compound on its degree of dispersion can be taken from analytical practice. When very dilute ferrous or ferric solutions are treated with an alkali sulfide, the result is not a black precipitate, but invariably a more or less intense green coloration. The latter is due to colloidally dispersed, *i.e.*, extremely fine, particles of FeS or Fe_2S_3. This colloidal dispersion is quite stable and it loses its color only on long standing, when a slight separation of a black precipitate occurs. If this sulfide precipitation from dilute iron solutions occurs in the presence of aluminum or zinc salts, the fine particles of iron sulfide adhere to the resulting $Al(OH)_3$ or ZnS, and thus have no chance to agglomerate with each other to produce coarser particles. As a result, the $Al(OH)_3$ or ZnS precipitate is tinted green, and thus looks quite like chromium hydroxide. This observation demonstrates the effect of an envelopment of coarser colorless particles by colored fine particles. The coloring of $Al(OH)_3$ or ZnS by means of tiny particles of iron sulfide is so characteristic that it can be used to reveal definitely the presence of even a slight quantity of iron in aluminum or zinc salts.

The interest of the analyst is not limited to the color differences exhibited by the same material in powders of different fineness. He must also take into account the color of mixtures consisting of powders of various colors and degrees of fineness. . Fink,[10] and also Briggs,[11] were the first to point out that the finer particles adhere to the coarser grains when they are mixed together, and hence the color of the finer powder may eventually predominate. For example, if coarsely powdered red iron oxide or Prussian blue, is mixed with finely powdered dolomite, the mixture will appear white. If, however, the red or blue powder is the finer and the white the coarser, then the mixture will appear red or blue. The following example illustrates how the differing degrees of fineness of the colored and colorless components can determine the color of a mixture of such powders. A dark grey mixture was obtained with 8 mg. of lamp black and 10 g. of dolomite when the latter was coarser than 40 mesh. If the dolomite was ground so that all of it passed a 200 mesh sieve, 654 mg. of lamp black, or 80 times as much, was required to produce

[10] C. S. FINK, *J. Phys. Chem.* **21**, 32 (1917).
[11] T. R. BRIGGS, *J. Phys. Chem.* **22**, 216 (1918).

approximately the same grey tint. The tendency of fine powders to adhere to the coarser particles of a second powder rather than to fill the voids between them is of considerable interest in the pigment industry. When an inert, cheap base (clay, barite, *etc.*) is mixed with an expensive dye, the finer particles of the dye are fixed on the surface of the more coarsely powdered carrier, whose color may thus be masked completely by a comparatively small quantity of the finer powder. In this way a colorless carrier, enveloped in a dye, can acquire the color value of a pure dye powder of the same particle size, and still act as a filler. The possibility that mixtures of colored materials may not exhibit the anticipated mixed colors but that the color of one ingredient may dominate, must be kept in mind not only in the examination of pigments, but quite generally when studying powdered, colored substances. In such cases, it is always necessary, by chemical tests, to determine whether a particular color is that of the entire sample, or whether only one of the components is responsible for the color. A masking of the color of coarser particles by the color of finer particles can result not only from mixing the powders mechanically, but also from precipitating the colored product of a chemical reaction on the surface of a colorless material. This method offers the possibility of forming a particularly dense envelope of particles fixed to the surface, and thus the tinting of the substratum will be more intense than that produced by purely mechanical mixing. A nice example of a coating produced by chemical action is found in the photohalides of silver. These are the light violet to cinnamon-brown products that quickly result when silver halides are irradiated. They owe their color to the free silver formed by photolysis: $AgHal \rightarrow Ag° + Hal°$. The very finely divided metal is deposited on the surface of the unaltered silver halide and gives it a uniform color. The various shades of the silver photohalides are determined by the extent of the irradiation, *i.e.*, on the absolute quantity of the free silver, and also by the particle size of the metal. Even traces of free silver are enough to give a strong coloration. Another example of superficial coloring by free silver is found in the reaction: $Ce^{+++} + Ag^+ + 4OH^- \rightarrow Ce(OH)_4 + Ag°$. A black precipitate is formed. It consists of bright yellow $Ce(OH)_4$ and finely divided silver, whose tinctorial power is so great that this reaction can be employed as a sensitive test for cerium[12] or ammonia.[13] If preferred, Mn^{++} ions can be substituted for Ce^{+++} ions. Analogous reactions can be carried out, in which other noble metal ions (Au, Pt, Pd, *etc.*) are reduced to the metal. All such reactions give deep black products that cannot be distinguished from each other by their external

[12] W. BILTZ and F. ZIMMERMANN, *Ber.* **40**, 4979 (1907).
[13] F. FEIGL, *Mikrochemie* **13**, 134 (1933).

appearance. Spot tests on paper, or identification spot tests on the solid sample, make frequent application of the superficial tinting of coarser materials by the finely divided colored products of chemical reactions. Such drop reactions often make it possible to detect very small quantities of colored soluble or insoluble reaction products (see Chapters X and XI).

Surface colorations of solids are not always the result of purely mechanical coatings. The particles of the carrier substance and those of the affixed material are sometimes held together by chemical forces. In fact, certain especially intense color effects are in this category. These will be discussed later in connection with the most important of all surface phenomena, namely, adsorption.

A distinct influence of particle size is evidenced in the settling of solids that are suspended in liquids of lower density, or that have been produced in such liquids by chemical reactions. The settling of solid particles that already have a definite form and retain this during the separation of the phases is known as sedimentation. The speed at which such solid particles settle in liquids, i.e., their sedimentation velocity, is expressed by Stoke's law. This involves not only the solid-liquid density difference and the viscosity of the liquid, but a further dominant factor, namely, the square of the radius of the particles. However, it should be remembered that Stoke's law applies rigidly only when the particles are not significantly affected by the actions of the solvent or the materials dissolved in it. Such effects, which will be discussed later, must certainly be considered with respect to solids that are formed under the conditions that obtain during analytical operations. Particle size determines not only the sedimentation velocity and the resulting sedimentation volumes, but also provides the possibility that the settling of solid particles may be arrested for longer or shorter periods. This delay may have analytical implications.

The settling of solid particles finds direct application in sedimentation analyses.[14] The rate of sedimentation and the sedimentation volume of aqueous suspensions are determined in such procedures. These data are important in the evaluation of certain technical materials, such as kaolin, cement, emery powder, insecticides, pigments, etc. Sometimes, the analyst separates the ingredients of a pulverized material by means of their differing sedimentation rates as a preliminary to a chemical examination of the sample. Occasionally, such separations can be made by elutriation, i.e., by subjecting the sample to a current of rising water and then removing the top layer. Obviously, both sedimentation velocity

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[14] Compare H. GESSNER, Die Schlämmanalyse, Vol. X of "Kolloidforschung in Einzeldarstellungen," Leipsic, 1931; see also the summary abstract by E. HOFFMANN. *Kolloid-Z.* **82**, 351 (1938).

and sedimentation volume are significant characteristics with respect to the detection of precipitates and their filtrability. One absolutely essential factor in sedimentation is that the solid particles be wetted by the liquid through which they are to settle. ·Wetting is the simplest example of the extremely important phenomenon that liquids can be held tenaciously on the surface of insoluble materials that are brought in contact with them. This retention, whose degree varies with different liquids and solids, is known as *lyosorption*, a term coined by Fodor.[15] As the name indicates, this is a special case of the phenomenon known as adsorption, which, in its most general form, can be defined as the concentration of a material on the surface of another material. Wo. Ostwald[16] suggested that the liquid film held by the surface of a finely divided solid be called the lyosphere. This liquid layer, which envelopes every individual particle, does not disappear, even after the particles have settled out. In other words, there is never a direct union or coalescence of the particles. Experiments[17] along this line have shown that the particles remain separated from each other by films of the liquid phase, often of considerable thickness. The thickness of this lyosphere is determined by the type of the surface and by the nature of the solid and the liquid phases. Lyosorption is most marked with heteropolar materials, and hence, it is probable that the activity of chemical (intermolecular) forces is responsible for the development of the lyosphere.

Lyosorption is responsible for the fact that if powders are shaken with liquids, in which they do not dissolve, and the suspension is then allowed to settle, the sediment occupies various volumes according to the nature of the moistening liquid. The volume of the sediment can be reduced by pressure or by centrifuging. It also becomes less at higher temperatures. Centrifuging the deposit produces a constant final volume, which also is smaller than the sedimentation volume, and which varies in the same·degree throughout the series of liquids. Lyosorption is also significant with respect to the sedimentation and centrifugation volumes of precipitates. Its degree depends on the nature and form-species of the precipitate, the temperature, nature of cosolutes, *etc.* Such factors must be taken into account in those quantitative semimicro and micro analyses in which small masses of precipitates are collected in calibrated centrifuge tubes, and the quantity of the precipitate then deduced from the volume of the centrifugate. For the reasons just given, the reference system used in such procedures must always be the

[15] A. FODOR, Grundlagen der Dispersoidchemie. Dresden, 1925.

[16] Wo. OSTWALD and W. HALLER, *Kolloidchem. Beihefte* **29,** 354 (1929).

[17] For literature see E. H. HAUSER, Colloidal Phenomena, p. 126. New York, 1939.

volume of centrifugates obtained from known amounts of precipitate, produced under conditions as nearly as possible like those that prevailed in the analyses.[18]

The possibility of arresting the settling of solid particles, or what is not necessarily the same thing, the preservation of their suspendibility, can have considerable analytical importance. A removal of the sedimentation ability was observed by Hofmann[19] and then by Reinders[20] in their detailed studies of the behavior of inorganic powders when shaken with water and an immiscible organic liquid (ether, benzene, *etc.*). In some cases the powder remained in the water layer, in others it passed into the organic layer, but usually it collected preferentially, or completely, in the interface between the two liquids. This variety in the distribution of solids between two liquids is determined by the nature of the solid and the liquids. It was explained by Bancroft[21] as follows: when a powder is shaken with water and an organic liquid, they may be adsorbed to different extents on the surface of the solid. If the adsorption of both liquids is sufficient to increase their miscibility on the surface, the solid will collect at the water-organic liquid interface. This accumulation, therefore, is always an indication of the common adsorption of the two immiscible liquids on the surface of the solid. If water alone is adsorbed, then the solid remains in the water after the shaking out. On the other hand, if the adsorption of the organic liquid is greater than that of water, the solid phase goes into the organic layer.[22] The localization or accumulation of solid particles in the interface between two immiscible liquids is similar to the flotation process, which is so widely employed to separate the components of various minerals.[22a] The pulverized mineral is suspended in water that contains agents which alter both the wettability of the particles and the surface tension of the liquid; consequently the buoyancy is also changed. A localization of particles in an interface can sometimes be utilized in analytical procedures. Fresh, and therefore finely divided, precipitates (organic or inorganic), that are not soluble in water or in an added immiscible organic liquid, can often be

[18] H. S. Greene, *J. Am. Chem. Soc.* **53**, 3275 (1931).

[19] F. B. Hofmann, *Z. physik. Chem.* **83**, 385 (1913).

[20] W. Reinders, *Kolloid-Z.* **13**, 235 (1913).

[21] W. D. Bancroft, *J. Phys. Chem.* **19**, 287 (1915).

[22] The Bancroft concept takes no account of the nature of the interface between the two immiscible liquids. This boundary area must have some influence, since it is decreased by the incorporation of solid particles. From the standpoint of surface tension, the requirement for accumulation of a solid in the contact surface of two immiscible liquids is that the surface tension prevailing there be greater than the surface tension of the solid toward each of the liquids.

[22a] Compare A. F. Taggart, Handbook of Ore Dressing, Section 12. New York, 1945.

made to collect in the interface if the suspension is shaken vigorously, and the layers then allowed to separate. A fine film is formed between the layers and is then quite discernible. In this manner it is possible to detect small quantities of colored or colorless precipitates, which otherwise are invisible or difficult to see if they remain distributed throughout the original large volume. This expedient is especially advantageous in case the organic liquid takes up colored organic reagents, which may interfere with the detection of small amounts of a colored precipitate. Shaking out then accomplishes both extraction and localization. This "analytical flotation" was applied by Feigl[23] who recommends it for the detection of minute quantities of precipitates. The increase in sensitivity of precipitation reactions that can be obtained by a manipulation as simple as this is really astounding.

For instance, Young[24] reported that nickel dimethylglyoximate can be made visible by shaking the system with kerosene, even though the ammoniacal nickel solution is so dilute that the addition of dimethylglyoxime produces no apparent change. A pink kerosene layer is formed, or more correctly a pink border of Ni-dimethylglyoximate develops at the kerosene-water interface. The precipitate also adheres to the glass wall that is wetted with kerosene.[25]

Belousov and Belousova[26] have studied particularly the use of analytical flotation for separating the components of a water suspension of a freshly formed precipitate. Among their findings are the following. A nickel dimethlyglyoximate precipitate, that is coated with hydrous ferric oxide, forms a coherent red film of the nickel-salt in the interface, when the suspension is shaken with isoamyl alcohol. If a suspension of hydrous alumina and ferric sulfide is treated with a little alizarin, and then shaken with amyl alcohol, a red foam is produced in the alcohol. Zinc sulfide remains in the water layer if a mixture of ZnS and Fe_2S_3 is

[23] F. FEIGL, Z. anal. Chem. 74, 380 (1928); F. FEIGL and H. LEITMEIER, Z. Krist. 40, 1 (1929). See also K. KERSCHNER and R. D. DUFF, J. Chem. Education 9, 1271 (1932); I. M. KORENMANN, Chem. Abstracts 34, 7208, 7775 (1940).

[24] R. S. YOUNG, Chemist-Analyst 34, 88 (1945).

[25] I. M. WINKELBLECH [Z. angew. Chem. 18, 1953 (1906)] made an observation that is closely related to the analytical flotation of suspended particles of a precipitate. He found that, if dilute gelatin solutions are shaken with benzene, a gelatin film separates at the H_2O—C_6H_6 interface. As little as 60γ gelatin can be detected by this means, but the sensitivity of this test is dependent on the pH of the solution. Since gelatin is colloidally dispersed in water, this instance indicates the possibility of separating colloidally dispersed materials by means of liquids that are not miscible with water. A. YANEK [Chem. Abstracts 15, 1239 (1921)] has actually demonstrated that the sulfides can be flocculated from colloidal dispersions of ZnS, CuS, and As_2S_3, and likewise collect in the interface, by shaking with benzene or chloroform.

[26] A. M. BELOUSOV and A. G. BELOUSOVA, Chem. Abstracts 29, 2469 (1935).

shaken with a large amount of chloroform. A mixture of arsenic, antimony, and tin sulfides, along with sulfur, is often produced in the qualitative scheme when the alkaline polysulfide solution is acidified. If the suspension is shaken with amyl alcohol and chloroform, only the finely divided sulfur stays in the water layer, while the sulfides collect in the water-alcohol interface. Unfortunately, these workers supplied no data regarding the quantities of materials that can be separated from each other by analytical flotation. Consequently, at present, it is not possible to make any definite appraisal of its practical analytical value as a qualitative separation procedure. The writer has investigated the special case of separating the acid sulfides from sulfur. He finds that a combination of flotation and extraction with carbon disulfide is preferable. This enables the analyst to detect very small quantities of sulfide, because the sulfur dissolves completely, and only metal sulfide remains in the water-carbon disulfide interface.

If a precipitate suspended in water collects in the interface when shaken with ether, chloroform, toluene, *etc.*, the same effect is obtained as though the suspension had been filtered. This fact was first recognized by Rothmund and Burgstaller[26a] who applied it in the Volhard titration of chloride. The removal of AgCl from the water layer made possible an accurate back-titration of unconsumed silver nitrate. As yet, not much use has been made in titrimetric procedures of this type of substitution for filtration.[26b]

Strictly speaking, such accumulation of solid particles in interfaces is not merely an arresting of sedimentation, but is rather a reversal of this process. If the particles are tiny enough, the interference with their aggregation into larger particles will also reduce their sedimentation velocity, and hence they will retain their suspendibility. This has great analytical significance, because the stabilization of a turbidity or a coloration due to homogeneous finely divided colorless or colored particles offers possibilities for qualitative detection and quantitative measurements. The arresting of a sedimentation, as well as the reverse, namely, the bringing about of settling from a suspendible condition, are closely allied to colloidal phenomena. These, because of their great analytical import, will be discussed as a separate topic in the following section.

COLLOIDAL RANGE, COLLOIDALITY, CHANGES OF STATE IN COLLOID SYSTEMS

The statements, in the preceding section, relative to the dependence of the solubility, color, and suspendibility of solids on their particle size,

[26a] V. ROTHMUND and A. BURGSTALLER, *Z. anorg. allgem. Chem.* **63**, 330 (1909).
[26b] M. B. SHCHIGOL, *Z. anal. Chem.* **91**, 182 (1932); Z. SHIBATA, *Chem. Abstracts* **32**, 881 (1938).

referred for the most part to particles that can be seen with the naked eye, and whose weight and volume are so large that all of the solid settles out in a relatively short time from its water suspension. Roughly speaking, the diameter of such particles is greater than 0.5μ. In contrast, the average dissolved, nonsettling, single or polymolecules, are of the order of $1\mu\mu$ in diameter. Theoretically, all particle sizes between these limits are possible. This range of dispersions (0.5μ to $1\mu\mu$), is known as the colloidal range. The dispersed particles may be solid (either crystalline or amorphous) or liquid. Their specific surface, i.e., the total surface/g., reaches enormous proportions, and this tremendous development and concentration of surface bring with them properties that can be quite different from those exhibited by compact solids, drops of liquids, or dissolved materials. Even solid particles, in which only one or two dimensions have reached the colloidal range (films, threads) may show such characteristic surface properties. The special chemical or physical behavior of materials in the colloidal range is known as colloidality. The upper and lower values of the dimensions in the colloid range should not be taken as strict limits for colloidality, because materials that are slightly above or below these respective limits often exhibit some colloidal properties. Furthermore, colloidality by no means remains constant within the bounds of the colloidal range, nor does it increase proportionally with the specific surface. Often there are optimum zones of colloidality; their location varies from system to system. It should be noted that colloidality always refers to a material plus its environment. Hence, strictly speaking, the terms colloid, colloidal range, and colloidality, should be used only as descriptive terms to define a physical system. For the most part, such systems are biphasic. The phase, whose degree of dispersion is the higher, is called the dispersed phase, and the medium, which surrounds the dispersed phase and is continuous, is termed the dispersion medium.[27] With extremely few exceptions, solid-liquid colloidal dispersions are the only ones that have any analytical significance.

The colloidal degree of dispersion of a solid in water can be reached from either direction. This also applies to dispersions of liquids, and to systems possessing nonaqueous dispersion media. In one case, compact portions of the solid, or its powder, are subjected to mechanical or

[27] It should be kept in mind, however, that this is absolutely correct only in so far as a colloidal dispersion is regarded as a heterogeneous system, in contradistinction to a molecular or true solution, which is taken as being homogeneous. An observer, whose dimensions were molecular, would regard a solution of sodium chloride as a heterogeneous system, since he would see its H_2O and NaCl molecules (or their ions) as separate phases. The limitations of our present methods and instruments justify our regarding a colloidal dispersion as a heterogeneous system, and a molecular solution as homogeneous.

chemical disintegration (dispersion). In the other case, a molecular dispersion is made to undergo aggregation of the molecules (condensation). The surface development brought about by the dispersion or condensation process can be represented by the continuous scheme:

$$\text{solid} \overset{I}{\rightleftharpoons} \text{colloidal dispersion} \overset{II}{\rightleftharpoons} \text{true solution}$$

in which $\overset{I}{\rightarrow}$ signifies dispersion and $\overset{II}{\leftarrow}$ condensation to colloid. The possibility of attaining a colloidal dispersion of solids by chemical methods, with participation of the dispersion medium and the materials contained in it, has analytical import. "Chemical" is used here in the broadest sense, i.e., it signifies both the occurrence of stoichiometrically defined reactions and also the consequences of the action of intermolecular forces. The transformation $\overset{I}{\rightarrow}$ in the case of many materials can be brought about even by the action of water, but usually auxiliary materials, contained in the water, are necessary to accomplish this dispersion. The process is then called peptization. It should be noted that $\overset{I}{\rightarrow}$ can be followed by $\overset{II}{\rightarrow}$, which means that peptization can be regarded as the preliminary stage in the production of a true, i.e., molecular dispersion. In fact, Traube[28] followed the solution of $HgCl_2$, K_2CrO_4, $K_3[Co(NO_2)_6]$ and other salts in water with the ultramicroscope. He found that a short period (1–2 minutes) of colloidal dispersion is traversed. Accordingly, it seems that a stage of colloidality is the general precursor of true solution, and especially in the case of difficultly soluble salts. Process $\overset{II}{\leftarrow}$, i.e., the condensation of a molecular dispersoid into the colloidal range, necessarily occurs whenever a precipitate is formed. Insoluble compounds, produced by a reaction of dissolved reactants, are doubtless formed initially in the molecular condition. This primary product then undergoes association to form an orderly or disorderly solid molecular system, i.e., a crystalline or an amorphous solid is produced. Consequently, the colloidal range of dispersion must be traversed before a visible precipitate appears. The life period of a colloidal dispersion may vary between wide limits, since its duration depends on the conditions attending the precipitation. Nevertheless, both transient and long-lived colloidalities are of great interest in analytical procedures. Various anomalies in analytical behavior can be attributed to a temporary colloidal condition, and numerous analytically important properties of materials are closely linked to their colloidal past. These points will be discussed later.

von Weimarn[29] was the first to point out that any material that is

[28] J. Traube, Kolloid-Z. **47**, 45 (1929).

[29] P. P. von Weimarn, Die Allgemeinheit des kolloiden Zustandes. Dresden, 1925.

formed by the interaction of two soluble reactants, and which is insoluble in a dispersion medium (water, alcohol, benzene, *etc.*), can be made to form the disperse phase of a colloidal system, provided the proper conditions are maintained. This "Weimarn precipitation rule" is an expression of the universality of the colloidal condition or, more precisely, of the fundamental possibility of obtaining as a colloidal dispersion, every solid material that is formed by the interaction of dissolved reagents. He showed in numerous cases that there are two formation-zones for the colloidizing of precipitates. The first is encountered when the reactants are highly diluted, the other if they are saturated. Colloidal dispersions are produced directly in the first case. Gels result in the second case, and these form colloidal dispersions when diluted with water. The zone of high dilutions is the more important in the formation of colloidal solutions during precipitation reactions used for analytical purposes. The observance of the validity of the Weimarn rule is especially important in gravimetric determinations. It is necessary to maintain such concentrations as will make impossible either an immediate formation of colloidal solutions or the production of colloid-soluble gels. Colloidal dispersions may also result in the region of intermediate concentrations if the conditions necessary for a stabilization of small particles exist or can be provided.

A solid-liquid system, in which a minute quantity of a solid, in the colloidal range, is dispersed in a large volume of liquid, with retention of the fluidity that is characteristic of the liquid, is called a colloidal solution, pseudo solution, or *sol*. Opposed to these systems are true solutions, which are systems containing the solute in molecular or ionic states of dispersion. Many physical properties of sols are of direct analytical significance. Among these, filtrability is preeminent. Colloidal solutions pass as readily as true solutions through filter paper, whose pores are 1.5–3.5μ wide, whereas particles larger than the pores are retained.[30] Ultra-

[30] Strictly speaking, the above statement applies only to the beginning of a filtration and not to its subsequent course. Because of its importance in analytical procedures, and because it is frequently not appreciated, it seems necessary to stress the point that filtration is by no means a simple operation. It is not governed solely by the size of the particles of a solid in relation to the width of the pores of the filter material. Other factors play a part. The most important of these are the adsorbability, form species, and consistency of the particles that are to be subjected to filtration. Thus, particles which are smaller than the pores of a filtering material can be adsorbed by paper fibers. As a result, the pores can become so narrow that a successful filtration can be made. In such cases, the precipitate "runs through" at first, and later it itself acts as a filtering medium. A striking example was furnished by A. SPRING [*Kolloid-Z.* **4**, 161 (1909); **6**, 11, 109, 164 (1909)], who worked with water suspensions of lamp black. Although the colloidal particles are smaller than the pores of the filter, they can be removed by filtration because the pores are constricted by adsorption. If some soap is added to the suspension, the particles of

filters, constructed from suitable organic gels and, hence, themselves colloidal in nature, allow true solutions to pass but hold back colloidal particles. Membrane filters, which can be prepared with various pore widths, will give clear filtrates with practically all sols, and by their aid even the finest turbidities can be removed quickly and completely. Pressure or vacuum is used with membrane filters.[31]

True and pseudo solutions also differ with respect to their osmotic properties. In true solutions, the osmotic pressure and all related phenomena (diffusion, vapor tension, depression of freezing point, elevation of boiling point, *etc.*) are simple functions of the molecular or ionic concentration of the solute. In colloid systems, the dispersed phase exerts very little, if indeed any, effect on the osmotic characteristics of the solution. Accordingly, molecular weights calculated from the osmotic data of colloidal solutions are exceedingly high, and should be taken as indicative of particle weights only.

The heterogeneity of colloidal solutions, that are produced during such analytical operations as the formation and washing of precipitates, can often be recognized directly by their turbidity or opalescence in incident light. Such turbidities are due to the fact that the dispersed phase and the dispersion medium have different coefficients of refraction, so that the light rays do not pass unhindered, but are bent laterally and deflected. If the particles are so small, or if their refraction differs so little from that of the medium that the particular dispersed system appears clear in incident light, its inhomogeneity can often be revealed by sending a small very intense beam of light through the liquid. The path of the ray will be luminous. Pure water and true solutions do not show this "Tyndall cone"; they are "optically empty." However, this test is not entirely decisive. On one hand, certain precautions are necessary to produce optically empty solvent water. On the other hand,

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soot adsorb soap, lose their capacity to be adsorbed by the paper, and consequently the suspension runs through the filter unchecked. Many precipitates composed of small particles behave analogously to lampblack, *i.e.*, after an initial period of running through, the subsequent portions filter well. On the other hand, some precipitates cannot be filtered, no matter whether the particles are smaller or larger than the pores of the filter. The reason is that the suspended particles have a slimy or gelatinous consistency. Consequently, they press against the paper and cover it with an impervious layer.

[31] In ultrafiltration the only certainty is that materials in true solution pass, and particles larger than the width of the pores of the membrane are held back. On the other hand, it cannot always be definitely decided whether the retention of particles is due to the screening action of the pores of the membrane, or whether the effect is the result, for instance, of an adsorption of the colloidal particles on the colloidal membrane. (See preceding footnote.)

quite a few colloidal dispersions (gelatin, albumin, silicic acid, *etc.*) give only a very faint Tyndall effect, and sometimes none at all.[32]

If a colloidal solution is examined under a microscope, the shape of the individual particles is not discernible because the limit of optical resolvability with an ordinary microscope is only of the order of 0.25μ. The shape of the smallest particles of the disperse phase will not be seen either when the brightest part of the Tyndall cone produced in a colloidal dispersion is viewed under a microscope, with dark field illumination. However, the diffraction disks produced by the individual particles will be visible provided there is sufficient difference in the refractive indices of the dispersed phase and the dispersion medium. This "ultramicroscopy" is successful only with very dilute colloidal systems; otherwise the diffraction images may overlap or entirely eclipse each other. These images do not remain stationary; the field of vision is filled with luminous and flashing points that are in constant motion. The "Brownian movement" of colloidal particles is thus made visible by the Tyndall effect. This phenomenon is not confined to particles within the colloidal range. Coarser particles, up to approximately 4μ in diameter, also show Brownian movement, *i.e.*, it can be observed in microscopically visible particles. The zigzag motion of such particles is due to their bombardment by the molecules of the enveloping liquid, which are in continuous and disorderly motion. Brownian movement is possible only if the particles are so small that the impacts received on one side are not compensated by the hits sustained on the opposite side, as is the case with larger particles. This explanation is supported by the fact that the intensity of the Brownian movement increases as the particles become smaller. The closer the latter approach to molecular dimensions, the more does the Brownian movement neutralize the action of gravity and interfere with the settling of the particles. Consequently, the Brownian movement is an important factor in colloidal solutions, because it tends to cause finely dispersed particles to distribute themselves uniformly throughout the liquid. It can be taken as a general rule that particles below 0.5μ are kept in permanent suspension by their Brownian movement.

[32] The principle of the Tyndall phenomenon is utilized in the nephelometric determination of a colorless precipitate, that can be kept in suspension, and whose quantity is too slight for an exact gravimetric determination. In the nephelometer, an intense beam of light is sent perpendicularly into the glass container, and the suspension is rendered opalescent by reflection and diffraction. The opalescence is compared with that produced by a standard containing a known quantity of the same suspended material. For literature on nephelometry see P. A. KOBER, *Ind. Eng. Chem.* **10**, 556 (1918); J. H. YOE, Photometric Chemical Analysis, Vol. II, Nephelometry (with contributions by H. Kleinmann). New York, 1929.

Fundamentally it might be expected that the Brownian movement of the solid particles of a colloidal solution would also tend to reduce the stability and homogeneity of the system. It causes the particles constantly to strike each other with considerable force. This might lead to a coalescence of the particles with the gradual production of larger aggregates, that eventually become too large to be affected by the Brownian movement, and hence they would settle out. An additional factor leading to sedimentation is the growth of the larger particles at the expense of the smaller, more soluble ones (see p. 433). The following considerations are also pertinent. The precipitation of materials is a process that always proceeds from systems with higher free energy and lead to systems of lower free energy. Consequently, it might be expected that all solid particles in the colloidal range, which are endowed with large free energies because of their tremendous surfaces, would spontaneously go over into the compact solid conditions that possess lower free energies. However, many colloidal solutions are quite stable. On the other hand, the production of colloidal solutions often demands precautionary measures that are very explicit for different materials and that vary from case to case. Hence, there must be very definite forces which oppose the union of the particles in the colloidal range and that tend to preserve this abnormal energy-rich condition. The explanation can be sought in the fact that the dispersed particles in colloidal solutions are never independent of the dispersion medium and the materials it carries in either true or colloidal solution. Definite relationships exist between the two phases. Since the chemical nature of the dispersed phase is a highly important factor in these relationships, colloidal dispersions of different materials in the same dispersion medium often behave quite differently in certain respects. Practically the only colloidal systems that are of interest to the analytical chemist are those in which water is the dispersion medium, *i.e.*, hydrosols, or the products that have resulted from them by the union (coagulation, flocculation) of the dispersed particles.

There are two main types of hydrosols: suspensoids and emulsoids. The solid residues obtained by removing the sol-forming water from suspensoids are called "hydrophobic colloids," whereas the corresponding partial dehydration of emulsoids produces "hydrophilic colloids." These terms are also commonly applied to the hydrated systems. The designation colloid is justified because it applies in all cases to surface-rich structures that show colloidality to varying degrees. The following summary gives the chief properties of two typical representatives of these main groups of hydrosols and their corresponding colloids:

Suspensoid Hydrosol	Emulsoid Hydrosol
(Hydrophobic or Irreversible Colloid)	*(Hydrophilic or Reversible Colloid)*
Example: Gold	*Example: Gelatin*
High molecular weight	High molecular weight
Non-diffusible	Non-diffusible
Optically non-homogeneous	Optically nearly homogeneous
Colored	Colorless
Non-viscous	Viscous even when dilute
Migrates in an electrical field	May or may not migrate
Osmotic effects slight	Osmotic effects slight
Cannot be prepared by direct solution	Prepared by direct solution
Stable only under certain conditions	Stable
Insoluble after coagulation	Reversibly precipitated and dissolved

This comparison shows that there are notable differences between the hydrosols of the types exemplified by gold and gelatin, respectively, and also between the residues obtained by coagulation or by evaporation of water. It should be emphasized, however, that no exact line of demarcation can be drawn between the hydrosols and colloids related to one or the other of the given representatives. Certain hydrosols and the solid products obtained from them do not fit completely in either of the groups, but display certain characteristics of both. Furthermore, colloidal solutions can be prepared which formally can be regarded as mixtures of suspensoid and emulsoid, but whose suspensoid characteristics are largely overshadowed by the emulsoid properties.

Most of the hydrosols of metals, metal oxides, metal sulfides, and salts are hydrophobic. They can never be prepared entirely free from electrolytes. Those essential to the preparation of suspensoid hydrosols, are called stabilizing electrolytes. On the other hand, after such hydrosols are once prepared, they, for the most part, are quite unstable against even minute quantities of electrolytes that may be subsequently introduced. The colloidal solution is flocculated by these added materials, and some of the coagulating electrolyte is invariably retained in the coagulum. This action, as well as the migration of the colloidal particles to one of the electrodes when a current is sent through the sol, is ascribed to the fact that the particles are electrically charged. Consequently, the particles behave, to an extent, as multivalent giant ions. The greater part of these charged bodies is made up of molecular aggregates of the dispersed phase, and the charge probably resides only in particular zones. There are two schools of thought concerning the structure of the particles of hydrophobic sols. According to one view linked with such names as Helmholtz, Gouy, and Freundlich, either cations or anions of the stabilizing electrolyte are adsorbed on the surface of the dispersed

molecular aggregate. If cations are adsorbed, the particles become positively charged, whereas the adsorption of anions confers a negative charge. Such adsorbed ions determine the potential and stability of the colloidal particles. The other attendant ionic species forms a diffuse layer around the adsorbed ions. In other words, this layer is not situated at a definite distance around the ions, but rather a concentration gradient is developed. This constitutes the "electrical double layer" of the stabilizing electrolyte. The ions which make up the outer portion of the diffuse layer that extends into the water are called the counter (contra) ions. It is usual to refer to the dispersed particles plus the whole double layer as colloidal particles or micelles. The dispersed particles plus that part of the double layer which moves with it in the electric current are called charged particles or charged micelles. The most important factor contributing to the stability of suspensoid hydrosols is the charge on the particles. Since they carry charges of like sign, they tend to stay apart. This repulsion opposes the mutual contacts resulting from the Brownian movement, whose potential agglomerating effect is thus reduced or nullified. The second viewpoint concerning the structure of colloidal particles is due to Duclaux, Thomas, and particularly Pauli. They regard the particles as a kind of polyvalent complex ion, in which a particular ionic species, by means of auxiliary valence forces, holds the molecular aggregates of the dispersed phase. This is somewhat analogous to the action of sulfide ions (S^{--}) and iodide (I^-) ions in polysulfides and polyiodides, where, by means of auxiliary valences, they function as carriers of sulfur and iodine molecules, respectively. However, these apparent analogues are actually quite different in several respects. In the colloidal particles, there is a wide disproportion between the carrier ions and the molecules of the neutral portion (see formulas on p. 453). Furthermore, depending on the experimental conditions, the composition of the particles may vary between much wider limits than is the case with the stoichiometrically defined polysulfides and polyiodides.

These two views of the structure of colloidal particles are by no means diametrically opposed to each other if the adsorption forces as well as the auxiliary valence bindings are regarded as intermolecular forces whose action always goes along with a definite orientation of the components that are joined to each other. This orientation appears to be the most important factor, and both views account for this orientation of the stabilizing electrolyte with respect to the neutral particles of the dispersed phase. Lottermoser[33] was the first to demonstrate clearly the significance of the electrolyte orientation. He used hydrosols of silver halides, and showed that either positively or negatively charged AgBr particles can be obtained when dilute solutions of silver nitrate and

[33] A. LOTTERMOSER, *J. prakt. Chem.* **72**, 39 (1905).

potassium bromide are brought together. If a slight excess of silver nitrate is used, Ag^+ ions of the $AgNO_3$ are adsorbed on bromine atoms of the AgBr surface. Conversely, if potassium bromide is in excess, Br^- ions of the KBr are adsorbed on silver atoms of the AgBr surface. An electrical double layer is developed in both cases. In the first instance, the stabilizing electrolyte is $AgNO_3$, in the second, KBr; while NO_3^- and K^+ ions function as the respective counter ions of the electrical double layer. Schematically, these oppositely charged colloidal particles can be represented by the general formulas $[(AgBr)_x..Ag]^+$ and $[(BrAg)_x..Br]^-$. Similar, non-stoichiometric coordination formulas can be set up for the colloidal particles of other hydrosols. It is important to note that the neutral portions of the dispersed phase in the hydrosol condition, and the products obtained from them, after removal of the dispersing water, are not necessarily disordered molecular aggregates, *i.e.*, amorphous materials. In many cases, X-ray analysis has proved that colloidal particles have a crystal structure.[34]

Some authorities have not accepted the concept that colloidal particles are stoichiometrically non-defined complex compounds of molecular aggregates and certain carrier ions.[35] A coordination chemical interpretation of the formation and behavior of hydrosols of the so-called semicolloids has met with less opposition. These materials are salts which, in very dilute water solution, dissociate into·the cations and anions corresponding to the formula of the salt. At higher concentrations, however, they do not undergo this simple ionic dissociation. Instead, one of the ionic species forms ion-like aggregates of colloidal dimensions. Accordingly, highly hydrated polyions, which exhibit an equivalent total electrical charge, are produced in place of the simple cations or anions. These polyions carry the electric current just as well as, or even better than, the single ions they have replaced. Such solutions accordingly act exactly like electrolytes with respect to conductivity. On the other hand, these ionic aggregates contribute just as little to the osmotic characteristics of the solution (boiling point elevation, freezing point depression) as colloidal particles do. McBain[36] has proposed the excellent term "colloidal electrolytes" for such materials.

[34] Compare H. B. WEISER, Inorganic Colloid Chemistry, Vol. 2. New York, 1935.

[35] It is difficult for many, when considering coordination formulas for colloidal particles, to harmonize the disproportion between carrier ions and large molecular numbers of the neutral portion with the customary simple formulation of complex compounds. This disproportion arises, however, only because schematically the entire particle is regarded as a nonstoichiometrically defined complex compound. If it were possible to differentiate those parts of it where there has been a direct binding of carrier ions to definite molecules of the disperse phase, then the numerical values of these combining partners would be simple.

[36] J. W. McBAIN, *Kolloid-Z.* **12**, 256 (1913).

Soap solutions, which he has studied for many years,[37] are excellent examples. For instance, sodium palmitate, NaP (P = $C_{15}H_{31}COO$), at low concentrations in water dissociates: $NaP \rightleftharpoons Na^+ + P^-$. At higher concentrations, the P^- ions agglomerate into highly hydrated colloidal particles, $(P^-)_n \cdot mH_2O$, in which n may have values from 10 to 20. At other concentrations, the system contains colloidal soap particles, $(NaP)_x \cdot mH_2O$. These remain combined with colloidal ions, and together they constitute the dispersed phase. The formation of hydrosols when semicolloids are put into solution can be pictured also as a result of surface dissociation. In this concept, molecular aggregates of colloidal dimensions are formed initially and some of their surface molecules dissociate. One of the ions remains bound to the other molecules and confers a charge on the entire aggregate.

Many other materials, including some of analytical importance, are included among the colloidal electrolytes. Examples are certain acid and basic dyes, indicators, silicates, tellurates, *etc.* In general, such materials have high molecular weights, or their individual molecules have an especially great tendency to polymerize in aqueous solution. As a rule, colloidal electrolytes show pronounced colloidality only in concentrated solutions. This means that the equilibrium:

$$\text{true solution} \rightleftharpoons \text{colloidal dispersion}$$

lies far toward the side of the colloidal particles only under such extreme conditions of concentration. Nevertheless, because of this equilibrium, even a dilute solution may sometimes behave like a colloidal dispersion in chemical reactions. Colloidal electrolytes are the bridge to the hydrophilic colloids, which, as it were, are the true-born colloids, since their solutions exhibit colloidality at all concentrations.

The hydrosols of typical emulsion colloids (gelatin, gum arabic, carbohydrates—many sugars, starch—tannins, *etc.*) show great similarity to true solutions, since, in contrast to many suspension hydrosols, no particular precautions are necessary to produce sols containing high concentrations of the dispersed phase. These materials, in conformity with their chemical composition, all form polyatomic molecules, being, in this respect, closely akin to the colloidal electrolytes. However, they often can be colloidally dispersed by merely bringing them in contact with water. To be sure this solution process is not the same in all cases. Some (sugar, tannin) dissolve even in the cold, while others (glue, gelatin) require warming. In certain cases (casein) it is necessary to add a little acid or base. Many emulsion colloids are especially char-

[37] J. W. McBain, Papers since 1911 in *Z. physik. Chem.*; *J. Am. Chem. Soc.*; *J. Chem. Soc.* Compare also P. Ekwall, *Kolloid-Z.* **77**, 320 (1936); **85**, 16 (1938).

acterized by their avidity for water, whose absorption is frequently accompanied by swelling. However, the volume attained in this swelling is always less than the sum of the volume of the dry dispersed material plus that of the imbibed water. This characteristic behavior shows that an intensive absorption and retention of water is an outstanding property of the emulsion colloids. It is assumed that the colloidal particles of hydrophilic colloids consist of polymolecules, enveloped by closely adhering films of water. This dense water-packing probably involves auxiliary valence action by the surface molecules or atoms of the dispersed phase. The enveloping film renders the colloidal particle quite similar to water and hence miscible with water. Likewise, the high viscosity, so characteristic of emulsoid hydrosols, may be related to the formation and retention of dense water envelopes. Because of the extensive hydration, the solid aggregate state of the particles loses its real significance as a separate solid phase. The particles, together with their accompanying water jacket, behave toward the dispersion medium (water) as though the system were of the liquid-liquid type, commonly called emulsions. In fact, the term emulsoid means "similar to an emulsion." The water jacket must be regarded as the principal stabilizing factor of hydrophilic colloids. This is shown by the fact that emulsoids lose their great stability if strong dehydrating agents are added. For example, alcohol makes gelatine solutions turbid; the original optically empty liquid then gives a strong Tyndall effect, especially if examined in the ultramicroscope.[38] Considerable amounts of alkali and alkaline earth salts flocculate emulsion hydrosols because of the withdrawal of water. In this case, it is more correct to view the effect as a "salting out," because the precipitated product redisperses in water if the salt solution is drained off.[39] Accordingly, agar solutions and the like, which have been treated with alcohol, are flocculated by even small amounts of electrolytes, because the alcohol has previously brought about a partial dehydration. Consequently, under such conditions, emulsoid hydrosols behave similarly to suspensoid hydrosols. The importance of water in the colloidal dispersion of these compounds is clearly shown in the case of tannin. Its water solutions are colloidal, whereas the osmotic data show that it forms true molecular solutions in glacial acetic acid.[40]

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[38] Compare H. R. KRUYT and H. G. B. DE JONG, Kolloidchem. Beihefte 28, 1 (1928).

[39] No account is taken here of an irreversible flocculation, caused by heavy metal salts (Ag, Cu, Zn), and producing precipitates that contain metals. Such coagulations involve the formation of adsorption complexes or so-called adsorption compounds (see p. 547).

[40] Compare E. NAVASSART, Kolloidchem. Beihefte 5, 299 (1913).

Even though the water envelope surrounding the particles is the most important stabilizing factor in the hydrosols of hydrophilic colloids, the electrical charges of the particles play a role here also. This charge arises either from the ions of the colloid itself, or from ions fixed on the colloidal particles. However, either H^+ or OH^- ions of the water can be bound. Consequently, emulsoid hydrosols likewise contain positively or negatively charged particles that can migrate under the influence of an electric current. The sign of the charge can be independent of the pH of the solution. Thus, gelatine produces a positive sol at pH < 4.7, whereas the sol is negative at pH > 4.7, that is, in weakly acid, neutral, or alkaline media. The pH value, at which there is no movement of the particles of an emulsoid hydrosol when a current is passed, is called the isoelectric point. The stability and viscosity of the hydrosol reach their lowest values at this pH, which shows that the charge of the particles plays a part in determining these properties. On the other hand, since the sol has a certain degree of stability at the isoelectric point, where the particles have no charge, it is evident that the charge is not the decisive factor in determining the stability of emulsoid hydrosols.

The differences in the behavior of the two extreme types of hydrosols are best understood if the following assumptions are made. In emulsoid hydrosols the hydration of the particles is more important than the electrical charge in conferring stability, whereas the latter factor is of prime significance in suspensoid hydrosols. However, there is no doubt that the particles of suspensoid hydrosols are hydrated, though to a lesser degree. The ions of the stabilizing electrolyte are hydrated and they consequently produce a water envelope that contributes to the stability of the colloidal particles. It should also be noted that the dispersed phase in many suspensoid hydrosols, in conformity with its chemical composition, is capable of coordinative binding of water molecules. This is especially true of metal hydroxides and oxides. Consequently, hydrosols of these compounds display properties that ordinarily are those of emulsoid hydrosols. Among these characteristics are: marked viscosity, decrease in stability on addition of alcohol (withdrawal of water), and activity as protective colloids (see p. 477).

The preceding statements concerning the structure of colloidal particles in hydrosols, and the factors that confer stability on these systems, lead to certain conceptions about the changes in state that can occur in colloidal systems. Such changes are of great interest in analytical procedures for the following reasons: (1) a state of colloidal dispersion always precedes the formation of a precipitate and influences its character; (2) the colloidal dispersion of reaction products can be preserved, and this may have either desirable or undesirable analytical consequences;

(3) certain insoluble compounds may be brought into the colloidal range of dispersion as sols through the action of electrolytes, or sometimes even of hydrosols; (4) precipitates can result from a mutual interaction of colloidally dispersed materials. Furthermore, processes which can affect the specificity, selectivity, and sensitivity of analytical tests and determinations may occur during the course of changes of state in colloidal systems in which the other materials present participate.

The passage of a material from its colloidal state of dispersion in a hydrosol into the state of aggregated particles, which are no longer spatially and dynamically independent, is often known as sol-gel transformation. The terms coagulation, flocculation, or pectization are also applied to this process, which is an important step in the formation of precipitates in analytical procedures. The reverse process, namely, the conversion of solid aggregates into the hydrosol state, is called peptization, deflocculation, dispersion, or, less aptly, colloidizing. The union of particles, which is the essence of coagulation, is governed by two factors: (1) the probability of collision and (2) the probability of adhesion of the particles. In other words, the particles must first meet each other, and the encounter must last long enough and be proper for further aggregation. The probability of a collision of particles depends on their Brownian movement, the concentration, and the temperature. In suspensoid hydrosols, the particles are protected by their charge and, in part, by a water envelope, which does not allow the spheres of the electrical potential to interpenetrate because of their like charge. The particles in emulsion hydrosols are predominantly protected by a dense water jacket. This functions as a buffer and practically eliminates the probability of adhesion. If no charges and no water envelopes were present, the great surface tension of the smallest particles and the force of their impacts would lead to a coalescence of the particles almost every time a collision occurs. Consequently, every decrease of the electrical charge of the particles, and every reduction of the water envelopes, must enhance the likelihood of adhesion. In suspensoid hydrosols, this probability attains values that are of practical significance, when the potential of the charge has fallen to a certain critical value. In emulsoid hydrosols, it is a matter of destroying the protective water envelopes that surround the particles and keeps them apart. When this happens, coagulation follows.

The coagulating action of electrolytes on suspensoid hydrosols has great analytical importance. The elucidation of these effects is due primarily to the work of Picton and Linder, Schulze, Hardy, and Weiser. Their studies, along with the findings of others, have led to the following important generalizations:

(1) The active precipitant in electrolyte coagulation is the ion whose charge is opposite to that borne by the colloidal particles;

(2) A portion of the active precipitant always remains in the coagulum;

(3) Certain minimum quantities of an electrolyte are required to bring about coagulation. The effect is not entirely due to the active ion; its corresponding contra-ion likewise plays some part in the coagulation;

(4) The coagulating effect rises with increasing valence of the active ion.

A picture of the coagulation process can be constructed either on the basis of the adsorption theory of the electrical double layer, or on the coordination chemical concept of the structure of colloidal particles. In the former, it is assumed that the counter ions of the electrical double layer are displaced by one of the ionic species furnished by the coagulating electrolyte. This exchange brings about a fundamental change (contraction) of the double layer and a loss of the electrolyte orientation, which is responsible for the potential and, hence, for the stability. If the colloidal particles are considered to be complex compounds that are not stoichiometrically defined, then coagulation is a chemical reaction between the particles and the coagulating agent resulting in the production of a quite insoluble, undissociated compound. It should be noted that an electrolyte which in small quantities stabilizes the colloidal particles, will bring about coagulation if large quantities are added. These effects of an electrolyte can be explained in the same way as just given, namely, contraction of the double layer or repression of the ionization of the colloidal electrolyte by the mass effect of ions of like charge. Both of these views[41] are consonant with the fact that colloidal particles can be discharged also by oppositely charged particles of another colloid. Therefore, hydrosols with opposing charges can undergo mutual flocculation. This effect actually is secured if the concentrations of the respective hydrosols are approximately equal. Otherwise, the suspensoid hydrosol which is in excess may exert a protective action against electrolytes, which normally bring about coagulation. The mutual flocculation and protective effects of suspensoid hydrosols will be discussed later.

The removal of the charge from particles of suspensoid hydrosols opens the way for the first stage of coagulation, namely, the initial adhesion of the primary particles to produce secondary particles. This

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[41] In truth, the process of coagulation is more complicated, as it also involves the adsorption of nonionized electrolytes and adsorption during the agglomeration of particles. This has been demonstrated in a series of careful studies by H. B. Weiser and associates (compare H. B. WEISER, Colloid Chemistry, pp. 231–239, New York, 1939).

does not signify that the colloidal dimensions have been exceeded at this point. Rather, it may be assumed that adhesion, at first, occurs only at isolated spots. The production of such localized adhesion products, which are usually referred to as colloidal aggregates, involves only a slight diminution in surface. Further aggregates can be formed from such secondary particles. The earliest of these have one or two dimensions still within the colloidal range. Eventually, particles entirely beyond this range are formed. It is common practice to denote as coagulation the process of particle aggregation up to the point at which the coagulum becomes visible, i.e., depending on its amount, up to the formation of a visible turbidity or of a filtrable precipitate. However, this designation involves an arbitrary cleavage. Particle aggregation admittedly is a process that sets in with great speed as soon as the colloidal particles are discharged, but it is by no means completed at the instant when the formation of a precipitate first becomes evident. Particle aggregation and modification of structure until a stable form is produced are brought about by physical processes that differ according to the nature of the dispersed phase. This aging process may take various directions: (1) enlargement of crystalline particles in all directions by orderly growth because of the higher solubility of the smaller crystals (this recrystallization is favored by the spatial proximity of the particles); (2) true coalescence of amorphous products; i.e., a union of particles similar to the flowing together of droplets; (3) transformation of disordered (amorphous) solid molecular aggregates into ordered (crystalline) solid molecular aggregates; (4) formation of clumps of amorphous or crystalline particles. Such physical processes may proceed concurrently. Dehydration may also occur during the aging, either by release of adsorbed water or, in the case of hydroxylated compounds, through the formation of anhydrides.[42] Finally, it should be remembered that analytical coagulation processes always take place in the presence of considerable quantities of cosolutes. There is a possibility that these may be adsorbed, not only when the particles are discharged, but also subsequently, and especially as long as the particles are still in the colloidal range. The variety of processes that may occur during an aggregation of particles makes it easy to see why the outward appearance of precipitates can be so very different. The designations crystalline, flocculent, curdy, amorphous, sandy, gelatinous, etc., express these differences.

[42] E. DAVIES [J. Chem. Soc. 19, 71 (1865)] observed that hydrous ferric oxide can be completely dehydrated by prolonged heating under water. Dehydration effects on aging, accompanied by changes in color, are exhibited by hydrated copper oxides (blue → olive green → brown → black).

Temperature often has a dominating influence in the coagulating and aging processes that determine the form of the product. Every analyst knows that many materials precipitated at room temperature cannot be filtered immediately because they pass through the filter. This is particularly true of crystalline precipitates. On the other hand, the same compounds can often be filtered off at once if they are precipitated at higher temperatures. This temperature effect is demonstrated well in the redox reaction between silver nitrate and hydrazine.[43] Non-settling metallic silver results at 16°C., while at 80–90°C. the precipitate is powdery.

It has been shown by X-ray analysis that the particles of many hydrosols, and also the seemingly amorphous coagula obtained from them, have a crystalline structure. Consequently, it is fair to ask why the form of an aggregation of particles is not generally and exclusively determined by the ordinary processes of crystal growth. This question cannot be answered with certainty at present. It appears, however, that one important factor responsible for the diversity of particle aggregation is to be sought in the fact that colloidal particles are not uniform corpuscles. The dispersed phase is inhomogeneous because of the stabilizing electrolyte, which is not entirely eliminated, even when the charge is removed, but is merely partially exchanged. The water envelopes that surround the flocculated particles likewise contribute to the inhomogeneity. This lack of homogeneity is probably the reason why particles can adhere only on certain spots or areas. The water envelopes (lyospheres) may possibly play a significant role here.[44]

There are various reasons why the process of particle aggregation is of analytical importance. It not only determines the perceptibility, form, and filtrability of a precipitate, but also influences its purity. Cosolutes that are fixed in the coagulum during the flocculation process would constitute an intolerable contamination, if they were not expelled as a result of the decrease in surface that accompanies aging. This self-purging of precipitates is particularly important in gravimetric determinations. The purpose of the usual procedure of allowing a precipitate to stand in its mother liquor for a while before filtering is not to complete the precipitation. If this were so, accurate volumetric determinations by means of precipitation reactions would not be feasible. The settling of precipitates accomplishes, above all, a growth of particles to a size that permits satisfactory filtration, and fortunately this is always accompanied

[43] A. GUTBIER, Kolloid-Z. 4, 308 (1909).
[44] Important insights into the process of particle adhesion have come from the very interesting considerations and experimental studies by A. VON BUZÁGH, Colloidal Systems, Chapter 6. London, 1937. See also A. v. BUZÁGH and coworkers Kolloid-Z. 76, 2 (1936); 83, 279 (1938); 84, 16 (1938).

by a self-purification. As a rule, precipitates are not allowed to stand for any length of time during qualitative analyses, and consequently serious errors often arise because of contaminated precipitates and loss of cosolutes. This point should be kept in mind when making group separations. The latter can often be profitably replaced by selective and sensitive identification tests for the individual components of the unknown solution. If the contamination of precipitates is attributed to adsorption, the self-purification becomes desorption, i.e., a reversal of adsorption. This reversal has been strikingly demonstrated in the adsorption system: mercuric sulfide—new fuchsin.[45] When the sulfide hydrosol is flocculated by means of this dye, the solution loses its color. However, on standing, the surface of the precipitate shrinks, part of the dye is released, and the supernatant liquid turns red. It can be assumed that all precipitates expel at least part of their adsorbed contaminants in this way on standing, although the effect is not always optically visible.

In a broad sense, every production of a precipitate from a true solution can be considered as a change of condition of a colloidal system. This follows from the fact that particles in the colloidal range must be produced during the passage of the reaction products from their initial molecular solution to the stage of a visible precipitate. If, as a consequence of coagulation and aging, the particles quickly reach a size beyond the colloidal range, colloidality is merely a transitory condition which leaves its imprint, at most, by eventual admixture of foreign materials in the precipitate. This remainder is primarily the consequence of the highly reactive and adsorptive surface of the particle aggregates while they are temporarily in the colloidal range. As a rule, those precipitated compounds which quickly traverse the colloidal range and rapidly overcome colloidality contain little or no water, and show a decided tendency to form crystalline aggregates. On the other hand, compounds that are capable of binding water, frequently form stable, coarse, highly hydrated colloidal aggregates. Such products, depending on their morphological peculiarities and physical properties, are called coagula, gels, or jellies. They all contain microcrystalline or amorphous particles embedded in water envelopes, with loss of the fluidity possessed by water or hydrosols. It should be emphasized that coagulation of highly dispersed systems in analytical processes is by no means the sole means of producing colloidal aggregates. They occur as such in nature. Certain water-free organic compounds (starch, cellulose, proteins, etc.) that are products of living matter, belong in this category. They are known as biocolloids.[46]

[45] H. FREUNDLICH and E. HASE, Z. physik. Chem. **89**, 417 (1915).

[46] Such organic compounds may be mixtures of macro molecules of various sizes, in which the constituents of the macro molecules are bound to each other by principal

Numerous rocks and minerals are coarse colloidal aggregates that originated in gels, and which have undergone solidification through aging over tremendous periods of time. These products of an inanimate nature are often the subjects of analytical examinations. Their color, water content, uniform distribution of accompanying materials, adsorptive powers, and other characteristic properties, that need to be considered in such studies, are often due to their colloidal character.[47]

Coagulation and aging processes that are active during the production of precipitates, are not the only changes in the state of colloidal systems that must be considered as important in analytical work. The reverse process of renewed colloidizing of flocculated colloidal aggregates must also be taken into account, as well as processes which can occur between materials in the colloidal range. The general term peptization is given to the process of forming sols from solids. Deflocculation is a better designation for the special case of the reversion of coarse colloidal aggregates to the hydrosol condition. Many precipitates, when filtered directly after they have been formed, partially revert to the colloidal condition on being washed with pure water. Familiar examples are sulfides, hydrous oxides, silver halides, stannic acid, and copper ferrocyanide. This peptizing occurs because the aging process has not yet proceeded far enough, and consequently the number of contact areas of the aggregated particles is still small. Accordingly, the adherent particles are again separable when the coagulating electrolyte is removed by the wash water, provided sufficient quantities of a stabilizing electrolyte are still present. Precipitates differ widely with respect to the extent of such deflocculation. This fact is understandable, because aging processes depend on the nature of the respective materials, the presence of cosolutes, and other conditions attending the precipitation. The familiar practice of allowing precipitates to settle, and to wash them at first not with water, but with a dilute electrolyte solution, provides both sufficient aging and an adequate amount of coagulating electrolyte. After the particles of a precipitate have been sufficiently enlarged through aging, so that the coagulation is no longer reversed by washing, then water alone cannot

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valences (molecular colloids). Another class is made up of micellar colloids, which are molecular aggregates that are held together by the action of auxiliary valences of the participating molecular species. Accordingly, these systems consist of either giant molecules or of molecular aggregates, both of colloidal dimensions. See A. LUMIÈRE, Colloides et Micelloides, Paris, 1933; H. STAUDINGER, Organische Kolloidchemie, Brunswick, 1941.

[47] Compare C. DOELTER's essay: Colloid Minerals in Colloid Chemistry (edited by J. Alexander), Vol. 2, p. 262 ff. New York, 1932. See also W. Lindgren's essay: The Colloid Chemistry of Minerals and Ore Deposits, in The Theory and Application of Colloidal Behavior (edited by R. H. Bogue), Vol. 2, p. 445. New York, 1924.

bring about peptization; a third material, a peptizer, becomes a necessary adjunct. This is peptization in the strictest sense. Excellent examples are provided by the solvent actions of alkali hydroxides on freshly precipitated hydrous oxides of Al, Cr, Zn, and ·on WO_3, SnO_2, SiO_2, etc. The formation of alkali aluminate, chromite, stannate, etc., must be taken into account here, in view of the amphoteric or acidic character of these oxides. It is quite likely that the anions of these compounds act as peptizers in the solutions finally obtained. There is no doubt as to the hydrosol nature of alkali silicate and stannite solutions.[48] The colloidal character of the green chromite solutions is quite decided. Such solutions not only can be freed of the colloidally dispersed hydrous chromic oxide by ultrafiltration, but a quantitative flocculation results if the solution is diluted and then boiled. Freshly precipitated, well washed hydrous oxides, particularly those of tri- and quadrivalent metals, are appreciably peptized by dilute acids. The H^+ ions act as the peptizer in such cases. Peptization can also be brought about by digesting with water solutions of the respective metal salts, which present the hydrolysis equilibrium: $Me^{+++} + 3H_2O \rightleftharpoons Me(OH)_3 + 3H^+$. The peptizing action in this case is due not only to the H^+ ions derived from the hydrolysis, but also to the other product of the hydrolysis, namely, the colloidally dispersed metal oxyhydrate (see p. 465). This is in agreement with the fact that hydrous metal oxides can also be peptized by foreign hydrolyzable metal salts; mixed sols result.[49] The peptization by means of metal salt solutions, with participation of their colloidally dispersed hydrolysis products, may be the cause of certain abnormal solution processes. · Thus, the induced solution of tin in nitric acid, in the presence of excess metallic antimony or iron (Chapter V), may be attributed to peptizing action. The hydrolysis products of the ferric nitrate, or the colloidally dispersed antimonic acid, may peptize the stannic acid initially formed. A further instance of this is provided by Ta_2O_5·aq, which is only slightly attacked by sulfuric acid and hydrogen peroxide. However, considerable quantities pass into colloidal solution if TiO_2·aq is also present. Obviously, the resulting pertitanic salts, or their hydrolysis products, act as the peptizing agent.[50] Other instances of peptization that have analytical interest include the following. Mundt[51] found that basic lead acetate can be detected in solutions of neutral lead acetate by adding hydrogen peroxide. A brown solution, obviously due to colloidal lead dioxide, results. Irindale[52] found that addition of sodium silicate to cobalt solutions produces a blue

[48] For literature see H. B. WEISER, Hydrous Oxides. New York, 1936.

[49] B. SZILLARD, J. chim. phys. 5, 488, 636 (1907).

[50] O. HAHN and H. GILLE, Z. anorg. allgem. Chem. 112, 283 (1920).

[51] W. A. MUNDT, Anales farm. y bioquim. (Buenos Aires) 1, 119 (1930).

[52] S. J. IRINDALE, Chem. News 130, 34 (1925).

precipitate of cobalt silicate, which dissolves in excess alkali silicate to form a blue solution. On treatment with chlorine or bromine water, the color changes to green-yellow, and then a black gradually develops. However, no precipitate of higher cobalt oxides forms; they remain colloidally dispersed. This procedure will reveal 5γ cobalt in 5 ml. solution, even when nickel is present.

Peptization may be closely allied to complex salt formation. This is seen in the solvent action of ammonia on the hydrous oxides of copper, cobalt, and nickel. Such solutions indubitably contain the respective metal ammine ions. However, at higher concentrations they exhibit hydrosol characteristics; for instance, they give a definite Tyndall effect. Another example is the ease with which Prussian blue (ferric ferrocyanide) is peptized by oxalic acid, a notably excellent complex-former with ferric ions. Such examples are cogent arguments in favor of regarding the building up of colloidal particles as manifestations of coordination chemical forces.

If every dispersion process that leads to the formation of colloidal dispersions solely by the action of solvent or dissolved materials is called a peptization, then the spontaneous solution of reversible colloids (*e.g.*, biocolloids, semicolloids) in water should also be viewed as peptization. This has a formal similarity to the process of true solution, which likewise involves active participation of the solvent and the materials that it holds in true solution. However, in one respect the two dissolution processes differ fundamentally. The attainable saturation in true solution is independent of the quantity of solute presented to the solvent while there is no such independence in the case of colloidal dispersion. Colloidal peptizability by water, dilute salt solutions, or even sols, may increase continuously with increasing amounts of dispersed material present, but generally it exhibits a maximum at medium amounts of dispersed material. This generalization, established by Ostwald[53] and Buzágh,[54] is usually called the "Bodenkörperregel," which is sometimes translated as "dispersed part rule," or "solid phase rule." In conformity with this rule, it is never possible to determine in advance the minimum effective quantities of a peptizing agent. The rule also signifies that optimal conditions for sol formation exist for a given peptizing agent and a given volume.

MUTUAL ACTIONS OF INORGANIC MATERIALS IN THE COLLOIDAL RANGE

The changes in the condition of colloidal systems resulting from a reciprocal action of colloidally dispersed materials may have important

[53] Wo. Ostwald, *Kolloid-Z.* **41**, 169 (1927); **43**, 225, 227 (1927); **50**, 65 (1930).

[54] A. von Buzágh, *Kolloid-Z.* **41**, 165 (1927); **43**, 215, 220 (1927); **48**, 33 (1929). Compare also J. Traube, *ibid.* **47**, 45 (1929).

analytical bearings. The action of hydrosols on each other is a case in point, and another is any mutual action displayed by colloidally dispersed materials during the course of coagulation processes. An excellent example of such mutual action is provided by the well known irregularities that are observed when chromic salts are treated with an excess of alkali hydroxide in the presence of certain materials.[55] The main reactants alone produce a transient precipitate, which then dissolves and forms a green solution of alkali chromite. Actually this solution contains also colloidally dispersed hydrous chromic oxide. If, however, the alkali is added to a chromic solution that also contains Fe, Mn, Mg, Cu, Co, or Ni ions, which of themselves can be precipitated as hydrous oxides, quite characteristic effects follow. If the chromic oxide is accompanied by Fe_2O_3 or MnO, in amounts less than 40% or 12% respectively, or by less than 20% of NiO or CoO, complete solution occurs. When the Cr_2O_3 is accompanied by more than 80% Fe_2O_3, 60% MnO, or 50% NiO or CoO, complete precipitation of $Cr_2O_3 \cdot aq$ takes place. Consequently, either induced solution or induced precipitation occurs, depending on the relative quantities of chromium and these accompanying materials. In the one case, the Fe_2O_3, MnO, etc., are kept in the colloidal state by the excess Cr_2O_3 hydrosol, whereas in the other case, coagulation of the oxyhydrates, now present in excess, causes coflocculation of the Cr_2O_3 hydrosol. Accordingly, both of these are instances of the reciprocal action of compounds in the colloidal range, leading in one case to peptization, and in the other to flocculation.

Another example of the mutual action of materials in the colloidal range is given by the reaction between sodium thiosulfate and warm solutions of aluminum salts. Hydrosols of opposite signs are produced and they mutually flocculate each other. The net equation:

$$2Al^{+++} + 3H_2O + 3S_2O_3^{--} \rightarrow 2Al(OH)_3 + 3SO_2 + 3S$$
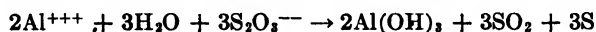
does not reveal the predominantly colloid chemical character of the precipitation. The reaction actually takes place in two essential stages:

$$Al^{+++} + 3HOH \rightleftharpoons Al(OH)_3 + 3H^+ \qquad (1)$$
$$S_2O_3^{--} + 2H^+ \rightarrow SO_2 + H_2O + S \qquad (2)$$
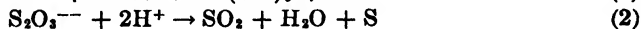
Eq. (1) represents the ordinary hydrolysis of aqueous aluminum salt solutions, which normally comes to equilibrium. A slight quantity of colloidally dispersed $Al(OH)_3$, which forms a positively charged hydrosol, results. Equation (2) represents the familiar decomposition of thiosulfates by acids. A negatively charged hydrosol of sulfur is produced

[55] Compare A. B. NORTHCOTE and A. H. CHURCH, *J. Chem. Soc.* **6**, 54 (1854); C. F. NAGEL, *J. Phys. Chem.* **19**, 331, 569 (1915); H. KNOCHE, *Kolloid-Z.* **67**, 195, 307 (1934); **68**, 37 (1934).

as a preliminary to the precipitation of aggregates of free sulfur. The H^+ ions produced in (1) are consumed in (2), and the resulting negatively charged sulfur sol flocculates the positively charged aluminum hydroxide hydrosol. Accordingly, the flocculation process involves only the colloidally dispersed $Al(OH)_3$ particles produced by disturbing the hydrolysis equilibrium and the colloidally dispersed sulfur particles. The quantities of these reactants is minute at the instant of flocculation and neither of them is present in great excess. This provides the setting for precipitation at extreme dilution, and hence for the deposition of a coarse-grained precipitate (see p. 627). Sodium thiosulfate actually does precipitate hydrous alumina in a granular form that filters well. This method has been recommended[56] as the basis of a quantitative method for aluminum. Salts of Cr, Ti, Th, and Zr behave similarly toward sodium thiosulfate, and the selective precipitation of the oxides of these metals by this reagent likewise involves a combination of hydrolytic and colloidal reactions.

The flocculation of colloidally dispersed positively charged hydrolysis products in solutions of metal salts is also involved in the carrying down of iron, aluminum, titanium, and zirconium when barium sulfate is precipitated. These coprecipitations were referred to on p. 149, in connection with the formation of complex metal sulfuric acids (sulfatoacids). Colloid chemical actions probably accompany these complex chemical effects. For example, positively charged colloidal $Fe_2O_3 \cdot aq$ can be precipitated from ferric solutions by means of negatively charged colloidal barium sulfate. (Analogous results are obtained in solutions of Al, Ti, etc.) It is significant that all the measures taken to repress the hydrolysis of ferric salts (low pH, reduction to ferrous state, masking of ferric ions) likewise cut down this coprecipitation of iron. Since the $BaSO_4$ particles remain in the hydrosol condition for only a very short time, the flocculation of oppositely charged colloidal particles of iron oxide is only an incidental reaction here, and does not dominate as in the precipitation by means of sodium thiosulfate. Nevertheless, the side reaction is sufficient to introduce considerable error in quantitative determinations of sulfate or barium predicated on the precipitation of pure barium sulfate.

The coprecipitation of oppositely charged colloidal particles can be distinctly increased if the precipitate remains in the colloidal range for a considerable time. An excellent illustration is found in the system: $Ti(SO_4)_2$-$Fe_2(SO_4)_3$. An acid solution of these sulfates contains colloidal dispersions of the hydrolysis products: $Ti(OH)_4$ and $Fe(OH)_3$. On

[56] W. GIBBS, *Z. anal. Chem.* **8**, 391 (1869). See also F. CHANCEL, *Compt. rend.* **46**, 937 (1858).

dilution and warming, the hydrolysis of the titanic sulfate is increased so markedly that $TiO_2 \cdot aq$ gradually deposits; in fact, the precipitation is quantitative when the proper conditions are provided. So much iron is coprecipitated from the mixed solution that the precipitate is not white but light yellow. Under identical conditions, a solution that contains only ferric sulfate remains clear and no precipitate of $Fe(OH)_3$ appears. This induced precipitation involves a union of positively charged $Fe(OH)_3$ particles with negatively charged $Ti(OH)_4$ particles. Accordingly, a white precipitate results when titanic salts are hydrolyzed in the presence of ferrous salts, which are only slightly hydrolyzed. Conversely, the hydrolytic deposition of $TiO_2 \cdot aq$ from solutions that contain hydrolyzable aluminum or chromium salts leads, as might be expected, to coprecipitation of aluminum or chromium.

If colloidally dispersed materials are treated with reagents that are in true solution, the reactions which would normally be expected usually occur.[57] This logically raises the question whether two materials in the colloidal range can also undergo mutual chemical reaction. Fundamentally, so far as hydrosols are concerned, the answer is in the affirmative. For instance, silver sulfide sols have been prepared by bringing Ag sols together with S sols,[58] and copper sulfide sols by mixing Cu sols with S sols.[59] Since direct reactions of solids far coarser than the colloid range have been observed in many instances, it is extremely likely that a colloidally dispersed material will react with another likewise colloidally dispersed substance. This applies not only to hydrosols, but also to materials that are in the colloidal range during and immediately after coagulation. The direct contact essential to such interaction is provided in cases of mutually coagulating particles at the places where the adhering particles touch each other. Reactions between hydrosols, and between materials that are in the colloidal range immediately following joint coagulation, sometimes give effects that are of interest in analytical chemistry. For instance, if hydrogen sulfide is passed into a weakly acidified solution of a zinc salt or alkali molybdate, that also contains free iodine, the usual gelatinous precipitate is not obtained. Instead, through the coprecipitation of sulfur, the precipitate is granular and filters readily.[60] It is remarkable that the precipitation of molybdenum sulfide is complete when iodine is present; in its absence the hydrogen sulfide must be used under pressure to secure this result. The

[57] If such reactions do not take place, it is because the normal reactivity of colloidally dispersed particles is sometimes hindered, or even prevented, by protective colloids. This colloidal masking is discussed on p. 474.

[58] H. FREUNDLICH and A. NATHANSOHN, *Kolloid-Z.* **28**, 258 (1921).

[59] E. SAUER and D. STEINER, *Kolloid-Z.* **72**, 35 (1935).

[60] Compare F. FEIGL, *Z. anal. Chem.* **65**, 25 (1924).

following reactions run concurrently when iodine is present along with the zinc (or molybdate):

$$I_2 + HS^- \rightarrow S^\circ + H^+ + 2I^-$$
$$Zn^{++} + HS^- \rightarrow ZnS + H^+$$
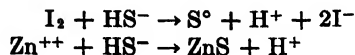
Since hydrosols of metal sulfides and of sulfur, in general, contain negatively charged particles, a mutual flocculation of the initially produced hydrosols is not involved here. However, a hydrosol reaction is possible:

$$ZnS \; (sol) + S \; (sol) \rightarrow ZnS_2 \; (sol)$$
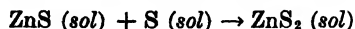
The resulting zinc polysulfide sol undergoes mutual precipitation with excess sulfur sol. Another possibility should also be noted. Zinc sulfide and sulfur particles in the course of their simultaneous coagulation may adhere to each other and remain adsorptively bound, a condition that is favored by the tendency to form polysulfide.

According to Komaretzkj,[61] another reaction in which colloidal sulfur participates is the action of alkali polysulfide or thiosulfate on acid solutions of stannous chloride. In the case of the polysulfide, the initial stage is the formation of a sol of stannous sulfide. The colloidal sulfur produced by the acid decomposition of the polysulfide then reacts with the colloidal stannous sulfide: $SnS + S \rightarrow SnS_2$. The resulting stannic sulfide is colloidally dispersed at first and then coagulates (possibly with addition of sulfur). Komaretzkj assumes that when thiosulfate reacts with acid stannous chloride solutions, basic stannous chloride or colloidal $Sn(OH)_2$ reacts with the colloidal sulfur produced by the acidification of the thiosulfate. The reaction: $Sn(OH)_2 + S \rightarrow SnS(OH)_2$ is followed, in acid solution, by: $SnS(OH)_2 + 4HCl \rightarrow SnS_2 + SnCl_4 + 4H_2O$. It is notable that polysulfide or thiosulfate, which normally function as reducing agents, bring about an oxidation in this precipitation of stannic sulfide from stannous solutions. The active agent is obviously the colloidal sulfur formed by the acid decomposition of these compounds.

The above mentioned production of zinc and molybdenum polysulfide, of stannic sulfide, as well as the formation of Ag_2S and CuS from hydrosols of their components, are clearly addition reactions that occur because of the union of molecules or molecular aggregates that are capable of independent existence. The realization of such addition reactions is surely much more likely in the colloidal range than double decompositions, that are to be regarded as reactions due to exchange of place. It may, therefore, be expected that addition reactions, particularly, will come under consideration when studying reactions between hydrosols, or between particles in the colloidal range during and after coagulation

[61] S. KOMARETZKJ, Z. anal. Chem. **69**, 257 (1926).

processes. The formation of addition compounds through the meeting of the reaction partners in the colloidal range cannot be demonstrated by the direct isolation of pure compounds. Such reactions never proceed alone; they are always associated with the aggregation processes of the reactants. A further consideration is that the particle aggregates do not enter the reaction *in toto*, but only at certain spots (contact areas). In general then, only the total product of concurrent partial processes can be obtained. However, it may be regarded as an indication of compound formation, if a mixture of two materials, that are precipitated together and which accordingly have gone through a hydrosol state and coagulation together, exhibits wide deviation in chemical behavior, as compared with the behavior of a mixture prepared from the same materials but precipitated separately. Numerous examples have been given in Chapter V to show that the action of coprecipitated metal sulfides toward solvents is often quite different from that of mere mixtures. Such reaction anomalies are by no means universal among coprecipitated sulfides, but are restricted to certain pairs of sulfides. This selectivity is strong evidence that union has occurred. An obvious assumption is to attribute the combination to the action of auxiliary valences of the sulfur atoms of the sulfides in the colloidal range. Such auxiliary valence action of atoms on the surface of solids plays a very important part in adsorption processes. Stable combinations produced 'by irreversible adsorption of molecular or colloidal partners on a colloid are called adsorption compounds. This designation was suggested by van Bemmelen. Adsorption compounds are discussed in more detail later. Reference is made there to a class of adsorption compounds whose formation is due to a union of positively charged hydrosol particles of metal hydroxides with negatively charged particles of a tannin hydrosol. This mutual flocculation is the basis of important qualitative tests and gravimetric methods for certain metals, in which tannin acts as the precipitant. Both of the materials in these precipitations react while in the colloidal state. Consequently, in principle, such precipitations are of the same type as the other reactions in the colloidal condition discussed in this section.

When sulfides are precipitated together, the formation of adsorption compounds through the union of the colloidally dispersed sulfides can only be detected by their abnormal behavior toward chemical agents. In contrast, certain oxyhydrates, which are quite similar to sulfides with respect to colloidality, provide examples in which abnormal color effects furnish direct proof of the reciprocal action of particles in the colloidal range. Tommasi[62] was the first to show that blue copper hydroxide,

[62] D. TOMMASI, *Compt. rend.* **99**, 38 (1884).

precipitated along with magnesium hydroxide (or certain other metal hydroxides), does not undergo the familiar color changes: blue → brown → black, but retains its blue color indefinitely at room temperature. This phenomenon has been studied by a number of investigators.[63] It doubtless is due to the fact that the dehydration process, $Cu(OH)_2$ → $CuO + H_2O$,[64] which is responsible for the color change, does not occur in the presence of magnesium hydroxide, *etc.* It seems plausible to assume that the colloidal particles of the $Cu(OH)_2$ and $Mg(OH)_2$ hydrosols react to form a relatively stable adsorption compound, or perhaps even $Mg[CuO_2]$.[65] Cobalt and nickel hydroxides, if precipitated together, show similar color anomalies.[66] Ordinarily the precipitate obtained by treating a cobalt salt with an alkali hydroxide is blue at first, but it rapidly turns violet and then pink.[67] This change is retarded by small amounts of nickel hydroxide formed simultaneously, the period of delay increasing with the quantity of nickel present. As little as 0.3% nickel still gives an effect in 10 ml. of 1 *N* cobalt solution. On the other hand, nickel hydroxide comes down as a green rather than the normal blue precipitate if cobalt hydroxide is coprecipitated. It is possible to detect as little as 1% cobalt in nickel salts by this effect. These color abnormalities no longer are of much practical significance for qualitative purposes, since more sensitive and specific tests for cobalt and nickel are now available, but nevertheless they may serve as guide posts for studies along other lines. They are included here primarily as directly apparent illustrations of the reciprocal action of particles in the colloidal range.

An instructive example of the mutual action of colloidally dispersed materials is furnished by the formation of "Purple of Cassius." It is produced as a red precipitate, or in dilute solutions as a hydrosol, by bringing together acidified gold solutions (chloroauric acid) with an acidified solution of stannous chloride. This reaction is the basis of a

[63] Compare H. B. WEISER, The Hydrous Oxides and Hydroxides, in Inorganic Colloid Chemistry, Vol. 2, p. 151 ff. New York, 1935.

[64] Actually, the dehydration process should be written:

$$CuO \cdot xH_2O \rightarrow CuO \cdot (x - a)H_2O + aH_2O$$

since the black oxide formed is hydrated.

[65] This assumption, which has not yet been tested experimentally, would be in agreement with the findings of H. J. M. CREIGHTON [*J. Am. Chem. Soc.* **45**, 237 (1923)] that solutions of $Cu(OH)_2$ in strong alkali hydroxides contain alkali cuproates, *i.e.*, CuO_2^{--} ions.

[66] S. R. BENEDICT, *J. Am. Chem. Soc.* **26**, 695 (1904).

[67] H. B. WEISER and W. O. MILLIGAN [*J. Phys. Chem.* **36**, 722 (1932)] proved by X-ray analysis that these two materials are not merely different hydrates or composed of different sized particles; rather they are two distinct forms of $Co(OH)_2$.

test for gold,[68] with the enormous concentration sensitivity, 1:100,-000,000. The reaction may be written:

$$2HAuCl_4 + 3SnCl_2 \rightarrow 2Au° + 3SnCl_4 + 2HCl$$
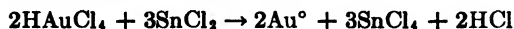
However, the precipitate is not pure gold, but contains much $Sn(OH)_4$. The latter can only have been formed by hydrolysis of the stannic chloride produced in the foregoing reaction. Consequently, a hydrosol of Purple of Cassius is a mixed sol, containing particles of both gold and stannic acid. The product formed by coagulation is called "gold purple." This elucidation is due to Zsigmondy.[69] He showed that the coagulation products obtained by mixing hydrosols of gold and stannic acid and then acidifying with nitric acid are almost identical with the Purple of Cassius formed by the analytical procedure. Silver-, platinum-, and palladium-stannic oxide purples are also known; they can be prepared similarly to gold purple. On the other hand, the familiar reaction: $HgCl_2 + SnCl_2 \rightarrow SnCl_4 + Hg°$, in which the conditions for the formation of a mercury-stannic oxide purple are factually provided, does not give this product. Instead, the precipitate consists entirely of free mercury. Therefore, the mutual action of colloidal particles that leads to the formation of a metal-stannic oxide purple is selective. Aqua regia does not extract gold from Purple of Cassius, neither colloidally dispersed or in aggregated form, nor does the gold react with mercury. Consequently it behaves as though it is not free gold, nor does it act as though it is present as a mixed coagulate with stannic acid; rather it seems to be combined with stannic acid. Its behavior is similar to the reaction anomalies encountered in the mixed precipitates cited previously. In line with its production from colloidally dispersed particles by mutual coagulation, Purple of Cassius can be logically regarded as a classic example of an insoluble adsorption compound.

The stannic acid in coagulated gold purple retains the characteristic of being peptized by dilute ammonia. Consequently, aggregated gold purple disperses in very dilute ammonia water and the gold remains colloidally dispersed. Thus the gold sol, which by itself is irreversible, forms a reversible hydrosol (see p. 451) in conjunction with the reversible stannic acid sol. Such stabilization of a sol and peptization is known as protective colloid action. The action of colloidal alkali chromite solutions in keeping particles of Fe_2O_3·aq, Al_2O_3·aq, etc., in colloidal dispersion (see p. 465) is fundamentally similar to the present case. The protective action of stannic acid hydrosols is not restricted to noble metals. Colloidal stannic acid can also peptize considerable amounts of hydrous

[68] T. K. Rose, *Chem. News* **66**, 271 (1892).
[69] R. Zsigmondy, *Ann.* **301**, 375 (1898).

ferric and chromic oxides. It has been found[70] that if these hydroxides are coprecipitated with hydrous stannic oxide, and the coagulating electrolyte then washed out, the residue is completely dispersible in very dilute ammonia. Studies[71] on the system $Fe_2O_3 \cdot aq$-$SnO_2 \cdot aq$ showed conclusively that complete peptization by ammonia is obtained only when an excess of stannic acid is present. Under the reverse condition, namely, if the $Fe_2O_3 \cdot aq$ is in excess, the peptization of the $SnO_2 \cdot aq$, and therefore the total peptization, is hindered. Accordingly, the relations here are quite similar to those prevailing in the peptization and precipitation in the $Cr^{+++} - Fe^{+++} -$ alkali system discussed on p. 465. It is remarkable, that, so far as is known now, the protective action of alkaline stannic acid hydrosols toward hydrous metal oxides is limited to $Fe_2O_3 \cdot aq$ and $Cr_2O_3 \cdot aq$. The protective action of $Fe_2O_3 \cdot aq$ hydrosols should be considered. A pertinent instance was referred to on p. 463, and as a further example, the action of $Fe_2O_3 \cdot aq$ toward $MnO_2 \cdot aq$ will be discussed [here. This protective action is shown when permanganate is added to a neutral solution containing ferric chloride and a manganous salt. The reaction:

$$3Mn^{++} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+$$
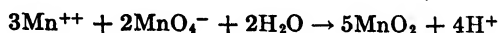
does not result in a precipitate of $MnO_2 \cdot aq$, but instead a stable, black-brown hydrosol is formed. Similarly, a ferrous chloride solution can be oxidized with permanganate without any precipitation taking place. The resulting brown solutions contain mixed sols, in which $MnO_2 \cdot aq$ is protected by $Fe_2O_3 \cdot aq$ hydrosols. It is, therefore, entirely possible that the decreased sensitivity of the ordinary sulfate test, when iron is also present (p. 71), is due in part to a protective colloid action and not entirely to the production of complex sulfato ferric acids.[72] The hydrosols of $Fe_2O_3 \cdot aq$ produced by hydrolysis may protect the $BaSO_4$ particles.

Holmes and Dietrich[72a] observed interesting anomalies that are the result of the peptization and protective colloid action of inorganic compounds. They found that passage of hydrogen sulfide into 0.5 N hydrochloric acid solutions of mercuric and cadmium chloride, which also

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[70] C. Lepez and L. Storch, *Monatsh.* 10, 283 (1889).

[71] H. B. Weiser, *J. Phys. Chem.* 26, 678 (1922).

[72] Since the sensitivity of the $BaSO_4$ precipitation is lowered also in solutions of hydrolyzable aluminum salts, there would be considerable interest in studies to determine whether precipitation reactions, in general, are less sensitive in solutions of metal salts which, though apparently indifferent, are subject to hydrolysis. If this is found to be the case, and if there is a relation between the hydrolysis equilibria and the lowering of precipitation sensitivities, it would indicate that the hydrosols of the respective hydrolysis products exert a protective action.

[72a] H. N. Holmes and M. A. Dietrich, *J. Am. Chem. Soc.* 48, 678 (1926).

contained an excess of chromic chloride, produced no filterable precipitation of mercuric or cadmium sulfide. Instead, stable black or yellow colloidal dispersions, which ran through the filter, resulted. Since chromic sulfate solutions have no analogous effect, and as it has been found that chromic sulfate solutions hydrolyze less than chromic chloride solutions, obviously the chromic oxide hydrosol resulting from the hydrolysis of the chloride acts as a protective colloid and keeps the mercuric or cadmium sulfide in a state of colloidal dispersion. With freshly prepared chromic chloride solutions, the effect appears when the ratio 2 Cr:1 Hg is exceeded. In solutions that have stood for 24 hours, and in which there has been extensive transformation of $[CrCl_2(H_2O)_4]^+$ into $[Cr(H_2O)_6]^{+++}$ ions, even a ratio of 1 Cr:3.5 Hg suffices to keep mercuric sulfide colloidally suspended. It is remarkable that ferric and aluminum chloride, whose solutions hydrolyze extensively to form colloidal $Fe_2O_3 \cdot aq$ and $Al_2O_3 \cdot aq$, do not interfere with the aggregation of mercuric or cadmium sulfide. Holmes and Dietrich also observed that the mercuric sulfide contains considerable quantities of chromium when it is prepared by passing hydrogen sulfide into chromic chloride solutions that contain a large excess of mercuric chloride. The peptization of mercuric sulfide by chromic oxide hydrosol, and the flocculation of this hydrosol by mercuric sulfide can be placed in parallel with the behavior, just described, of the systems $Cr_2O_3 \cdot aq$-$Fe_2O_3 \cdot aq$-alkali, and $SnO_2 \cdot aq$-$Fe_2O_3 \cdot aq$-ammonia, in which, likewise, according to the excess of one of the components, either peptization or coprecipitation results.

Other examples can be cited to illustrate this ability of inorganic hydrosols to exert protective colloid and peptization effects that enter into analytical procedures. It has been known for a long time[73] that ammoniacal solutions of copper oxide, which, in addition to cuprammine cations, contain colloidal $Cu(OH)_2$ particles (see p. 464), can peptize freshly precipitated $Cr_2O_3 \cdot aq$. This is the reason why it is not possible to accomplish a clean-cut separation of copper from chromium by precipitation with excess ammonia, or by digesting the coprecipitated hydroxides with ammonia. Peptization and coprecipitation in the colloidal range are further illustrated by the behavior of mixed molybdate and tungstate solutions toward uranyl salts.[74] Molybdates do not react with uranyl salts, whereas tungstates are quantitatively precipitated. If, however, the molybdate, which is partly present as a semicolloid, is in excess, the tungstate precipitate does not form. Conversely, when a mixture containing excess tungstate is treated with uranyl salts quantitative coprecipitation of the molybdenum occurs. The prevention of the

[73] M. PRUDHOMME, *J. Chem. Soc.* **25**, 672 (1872).

[74] F. R. HITCHCOCK, *J. Am. Chem. Soc.* **17**, 490 (1895).

precipitation obviously is due to a peptizing action of the molybdate; the coprecipitation of the molybdenum clearly involves its adsorption on the coagulating uranyl tungstate.[75] Extensive coprecipitation of $MoO_3 \cdot aq$ also occurs when $WO_3 \cdot aq$ is precipitated by acidifying a Na_2MoO_4-Na_2WO_4 solution.[76]

Many of the reaction anomalies cited in this chapter were classified as instances of induced solution and induced precipitation (see Chapter V). They were explained as being the results of peptization and changes of condition in colloidal systems, in other words, as consequences of the particular properties of colloidally dispersed materials. The peptization of $Fe_2O_3 \cdot aq$ or HgS by Cr_2O_3 hydrosol, or the peptization of $MnO_2 \cdot aq$ in hydrolyzing ferric solutions, can be designated as other instances of masking also. However, it is not the formation of Fe_2O_3, HgS, or MnO_2 that is masked, but the visible precipitation of these materials. Likewise, the term masking can be applied to the non-occurrence of the usual reactions of the constituents of coprecipitated products, which have coagulated together from the hydrosol state. Many instances were given in Chapter IV of masking of reactions, that are known to be due to the formation of stoichiometrically defined complex compounds, or their ions. The maskings cited in the present chapter differ from such complex maskings in that their fundamental feature is the occurrence of colloid chemical processes, and not the production of definite complex compounds. Consequently, the phrase "masking through colloid phenomena" or, in short, "colloid masking" is justified for purposes of distinguishing and characterizing this effect. Pertinent examples, that have analytical import, will be discussed later.

Certain types of induced precipitations can be considered from the standpoint of a change in condition of colloidal systems and a mutual action of materials in the colloidal range. This phenomenon was discussed in Chapter V, where numerous examples were given. The term "induced" is applied to a precipitation reaction that does not take place when a material is by itself, but which proceeds, to varying degrees, if certain of its cosolutes are brought down simultaneously by the same precipitant. The latter reaction is called the inducing or primary

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[75] Since the systems Cr_2O_3-Fe_2O_3, Cr_2O_3-MnO, SnO_2-Fe_2O_3, Fe_2O_3-$BaSO_4$ exhibit an analogous behavior, this points to the following relationships: Small amounts of a precipitate formed together with a hydrosol, can be peptized by the hydrosol. Larger quantities of the same precipitation product bring about partial flocculation or adsorption of the colloidally dispersed particles of the hydrosol. Perhaps this is a general mode of behavior that must be considered in analysis. However, further conclusive experimental evidence is not available.

[76] L. WÖHLER, Z. Elektrochem. 16, 693 (1910); L. WÖHLER and W. ENGELS, Kolloidchem. Beihefte 1, 459 (1910).

precipitation, in distinction to the induced or secondary precipitation. Experience has proved that various processes may be held responsible for induced precipitations. They include: catalysis reactions, formation of complex salts, production of mixed crystals, and adsorption processes of various kinds (post-precipitation, adsorption compounds, *etc.*). A special kind of induced precipitation may occur in solutions that are so dilute that the addition of a precipitant does not result in the production of a visible precipitate, though an immediate precipitation occurs at higher concentrations. It is sometimes possible in such solutions to bring about a quantitative deposition of the nonprecipitable traces by precipitating a sufficient amount of a cosolute. The latter then is called a collector, and the effect is termed a collector action of the primary precipitation. The production of highly dispersed particles and their surface actions are involved in these induced precipitations of traces. The following considerations hold in such cases. When a precipitation reaction is undertaken in a solution, the precipitate never appears immediately after its solubility product has been exceeded, but only after some higher concentration is reached. This means that the reaction product has already been formed before the threshold of visibility of the precipitate is passed.[77] During the period preceding the visible appearance of the precipitate, the material is present either in a supersaturated solution, or all or part of it has passed from this precolloidal dispersion into a hydrosol state. The stability of such particles with highly developed surfaces is particularly great in precipitation reactions carried out in concentration ranges that are not too far from the values fixed by the solubility product. If then, the same precipitant forms another precipitate in a milieu of this kind, the particles of this second precipitate will likewise pass through the precolloidal and hydrosol states, and subsequently coagulate. The resulting coarser particles will have colloidal dimensions, at least at the beginning of the aging. Consequently, it is possible to have a mutual action between particles of various materials in both the precolloidal and hydrosol conditions. Furthermore, reaction products that are passing out of the hydrosol condition may be active both during and after the coagulation. In the precolloidal stage, it is possible for particles of the one type of combination to function as crystal nuclei for the second type of combination. The result may thus also be the formation of mixed crystals, a process in which the determining influence is the radius of the precipitable ions, since only ions of approximately the same radius can mutually replace each other in a crystal lattice. The coprecipitation of traces of titanium when zirconium is

[77] This can be simply but clearly demonstrated in certain cases. Compare F. FEIGL, *J. Chem. Education* **20**, 241 (1943).

brought down by arsenate from acid solution is probably a case in point, and likewise the retention of potassium permanganate by freshly precipitated barium sulfate. (Compare Chapter V.)

Another action, possible in both the precolloidal and hydrosol stages, is the realization of addition reactions through the operation of valence forces emanating from the particles of the dispersed material. The formation of principal valence compounds must be taken into account of course, but the production of complex compounds, using the term in its widest sense, through the action of auxiliary valences is of special importance. The formation of a principal valence compound is very probably the reason for the collector action exerted by tellurium when stannous chloride (or other strong reductants) are added to a solution containing gold, platinum, palladium, *etc.*, along with a tellurite.[78] Solutions of the platinum metals on treatment with stannous chloride produce platinum purple *i.e.*, platinum metal hydrosols protected by stannic acid (see p. 471). If the reduction of the noble metal salt is accompanied by a reduction of the tellurite to free tellurium, the latter reacts with the noble metal and forms a telluride. This salt adheres to the surface of the free tellurium which is passing from the hydrosol condition into a coagulum. Thus the telluride is removed from the solution. Amounts of noble metals that are too small to form a visible quantity of a purple can be precipitated in this way along with a relatively small quantity of tellurium. The deposit can be collected, and, after ignition and volatilization of the tellurium, is available for qualitative or quantitative examination. Many examples of collector action were cited in Chapter V. However, the great majority of such effects do not involve the products of redox reactions. Most of the known instances have been observed among sulfide and hydrous oxide precipitates, *i.e.*, among compounds that frequently exhibit colloidality even after coagulation from the hydrosol condition, and which furthermore are capable of auxiliary valence action by virtue of their sulfur and oxygen atoms. It appears as though compounds that are immediately precipitated in a visible crystalline form are, in general, less capable of collector action than compounds which, like the sulfides and oxyhydrates, come down in an amorphous, gel-like form.[79] Such latter compounds, which provide a relatively slow primary precipitation, and whose particles, accordingly, retain colloidal dimensions over a comparatively long period, may be expected to exhibit better collector action than those in which the primary precipitation quickly

[78] S. Kuehnel-Hagen, *Mikrochemie* 20, 180 (1936).

[79] For example, J. H. Yoe and L. G. Overholser [*J. Am. Chem. Soc.* 61, 2058 (1939)] found that Ni dimethylglyoximate has no appreciable collector action toward Pd dimethylglyoximate which has the same crystal form. The writer has observed that Sb pyrogallate and Bi pyrogallate (see p. 177) exhibit no mutual collector action, even though they have the same constitution and crystal form.

traverses the hydrosol condition. However, comparative experiments designed to test this conclusion have not been made as yet.

The concept accepted here places the collector action in induced precipitations in the precolloidal and hydrosol stages of the primary and secondary precipitation. In agreement with this is the fact that appreciable collector action is exerted by precipitates almost exclusively while *in statu nascendi*. Products that have already been thrown down, and which thus are aging or have aged, show no, or a smaller, collector action. This is particularly true of crystalline precipitates; amorphous precipitates retain a collector effect much longer. The use here of the terms precolloidal and colloidal dispersion admittedly involves an arbitrary division, since no definite boundaries between these stages can be established. Consequently, there is no way of determining the extents of the reciprocal action of particles of various materials in one or the other of these stages. However, it is of fundamental importance that the tremendous surface of particles in both these degrees of dispersion has a decisive influence, and so the inclusion here of this type of induced precipitation is justified.

The collector action of precipitates *in statu nascendi* may have high importance in analytical procedures, particularly in trace analysis. Frequently, the task is not merely to detect and determine materials that are present all alone at great dilutions. More often, the problem is to detect traces of an accompanying material or contaminant in a material that is uniform in all other respects. In such tests of purity a direct application of even the most sensitive reactions fails because of the abnormal limiting proportions and the especially great dilutions. Frequently the only feasible method is to produce a precipitate that has appropriate collector action. The traces of material that are thus localized can be subjected to identification tests or colorimetric determinations, either after removing the collector, or sometimes even in its presence.[80] Obviously, the best results will be given by those precipitation reactions in which even small amounts of precipitate exert large collector action. Consequently, the search for suitable collectors has become a very important factor in the development of qualitative and quantitative inorganic microanalysis. No studies have been reported regarding collector actions that could be applied in organic analysis.

PROTECTIVE COLLOID AND PEPTIZATION ACTION, COLLOID MASKING AND SENSITIZATION BY ORGANIC COMPOUNDS

The discussion in the preceding section of the analytically important interactions of materials in the colloidal state and colloidal range dealt

[80] Compare, E. B. SANDELL, Colorimetric Determination of Traces of Metals. New York, 1944.

almost exclusively with inorganic compounds. Among others, examples were cited of the stabilization of a colloidal dispersion by another colloidally dispersed material (protective colloid). Special interest attaches to the stabilization of a colloidal dispersion of materials by organic compounds that are themselves in the colloidal state. Instances are sometimes also encountered here of a diminution of the reactivity of colloidally dispersed materials. This effect will be called colloid masking to stress the special contribution to it of colloid-chemical factors. Many organic materials that can stabilize the colloidal dispersion of certain substances occasionally can also bring about the opposite effect, namely, the aggregation of colloids. This is known as sensitization. It will be pointed out that numerous materials which are insoluble or only slightly soluble in water can likewise act as sensitizers. Both protective colloid and peptization actions, as well as the colloid masking and sensitization brought about by organic compounds, are so important to the specificity, selectivity, and sensitivity of tests that a separate discussion here is justified, even though the relevant examples to be cited here would have fitted well in the section devoted to mutual action in the colloidal range.

The peptization and protective colloid effects cited in the foregoing discussion were exerted by metal oxide hydrosols that contain highly hydrated colloid particles. These hydrosols, as shown by their relatively great stability against electrolytes, are closely allied to the emulsoid hydrosols, in which the extensive hydration of the particles is plainly evident. Therefore, particularly strong effects would be expected of typical emulsion hydrosols. This anticipation is actually realized. Many organic colloids, which are readily peptized by water, show such marked effects that they are commonly referred to as protective colloids. Among them are: the biocolloids, such as albumin, starch, sugar, rubber, mucins; hydrolysis products of albumin (lysalbinic and protalbinic acids); hydrolytic products of starch (dextrins); saponins; soaps. Such protective colloids have considerable importance as auxiliary reagents, because they make it possible to peptize solids that have been flocculated, and furthermore they can confer resistance against flocculating agents on colloidally dispersed materials. This latter effect is applied in analysis. If reactions that result in insoluble colored or colorless products are carried out in the presence of adequate amounts of a suitable protective colloid, the usual transitory hydrosol stage of the precipitation product is stabilized. Hydrosols protected in this manner may then be utilized in colorimetric and nephelometric determinations. As a rule, reliable stabilization of the sol form is obtained only by precipitation from dilute solutions.[81] Presumably, large amounts of electrolytes decrease the protective effect.

[81] Protective colloid action is often regarded as being the same as peptizing action.

The action of protective colloids was formerly attributed to a purely mechanical effect, namely, the coating of the particles of a suspensoid (hydrophobic) colloid by the highly hydrated particles of an emulsoid (hydrophilic) colloid.[82] This concept must be supplemented and extended. In the first place, it has been found that protective actions are often definitely selective. Their extent depends not only on the nature of the protective colloids employed, but also on the nature of the materials to be protected. Furthermore, in the case of gold sols protected by stannic acid, it was shown that SnO_2 particles are capable of a protective action even when they are far larger than the protected gold particles. In such instances there is no enveloping protection but, instead, an adhesive protection.[83] In other words, the gold particles are protected against aggregation solely through their being fixed on the SnO_2 particles. Consequently, a likely supposition is that an effective protection through envelopment or firm attachment of particles in the colloidal range comes about only because the participation of binding forces between the particles of protective colloid and those of the hydrosol to be protected leads to the union of the particles. Such combinations are probably quite similar to adsorption compounds. They may, in a sense, be regarded as adsorption compounds in a stable colloidal state, in which the hydrophilic constituent acts as vehicle for the pseudo-solubility of the hydrophobic constituent. This action, is related to the hydrotropic dissolution of materials discussed in Chapter VIII. However, it must not be forgotten that, when protective colloids are applied to analytical purposes, their action does not begin merely when a precipitation product reaches and traverses the colloidal state. The protective colloids are present through all the stages of the genetic formation of the material (see Chapter XI) that precede the colloidal state, and thus can act on insoluble materials in the pre-colloidal stages.[84] The

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This is not quite correct. Peptization and deflocculation signify the conversion of a solid product to its hydrosol form, whereas protective action means stabilization of the colloidal degree of dispersion. These should be thought of as separate processes, although it is frequently difficult to differentiate them with certainty. In practice, the difference between maintenance and production of a sol is often shown by the fact that the preliminary addition of a protective colloid to a reacting system can result in the complete stabilization of a precipitate in the sol state, whereas, if the same precipitate is coagulated and then treated with a like quantity of protective colloid as was used in the other case, either none, or only a part, of the precipitate will be transformed to a sol.

[82] Compare H. BECHHOLD, Z. physik. Chem. **48**, 385 (1904).

[83] P. A. THIESSEN, Kolloid-Z. **101**, 241 (1943).

[84] Compare E. G. HEDGES and R. V. HENLEY, J. Chem. Soc. **129**, 2718 (1928); T. R. BOLAM, Trans. Faraday Soc. **24**, 463 (1928); **26**, 133 (1930). For further literature see H. B. WEISER, Inorganic Colloid Chemistry, Vol. 3, p. 88. New York, 1938.

following possibilities arise: (a) Adsorption by the protective colloid of simple or polymolecules of a compound produced by a chemical reaction. In this way, the formation of nuclei as well as the growth of nuclei can be prevented and these processes are responsible for the development of a new phase (compare Chapter XI). (b) Furthermore, the protective colloid itself may act as nuclear material for the deposition of a new phase, which then remains in combination with the protective colloid. (c) One of the participants in a reaction that proceeds in the presence of a protective colloid may be adsorbed on the latter and react in this adsorbed form. Accordingly, an adhesion of a reaction product to the protective colloid becomes explicable. Therefore, it is probable that a protective colloid action, occurring under analytical conditions, need not be a uniform process. It may consist of an interplay of concurrent and successive partial processes, that proceed to varying extents. However, the most important process is doubtless the prevention of an aggregation of the particles.[85] At present, no definite predictions can be made as to which protective colloids will be most effective toward precipitates formed in their presence, because the protective agents may and do act in such a variety of ways. Empirical trials and the experience gained in analogous cases are the only available guides.[86] Nevertheless, it should be emphasized that protective action can be secured not only with colloids derived from natural products, but also with their degradation products, such as protalbinic and lysalbinic acids.[87] These latter suggest

[85] The hindering of a growth of particles, or of a transformation to a stable modification, by protective colloids, can be plainly seen in the case of mercuric iodide. This compound, if formed by the union of Hg^{++} and I^- ions, comes down as a yellow microcrystalline precipitate, which rapidly turns red. If the precipitation occurs in the presence of gelatin or egg albumin, a yellow hydrosol, stable even to heat, is obtained. In contrast, agar agar has little or no stabilizing effect on yellow mercuric iodide. Compare B. KISCH, *Kolloid-Z.* **49**, 433 (1929).

[86] The hope that Zsigmondy gold numbers might be used to evaluate the analytical effectiveness of protective colloids has proved false. The gold number is defined as the maximum number of milligrams of a protective colloid that may be added to 10 ml. of a standard gold sol (*ca.* 0.005% Au) without preventing a color change (from deep red to violet) when 1 ml. of 10% NaCl solution is added rapidly [R. ZSIG-MONDY, *Z. anal. Chem.* **40**, 697 (1901)]. As stated, protective action is often selective. Accordingly, it is understandable that such an action, which hinders an aggregation of gold particles within the colloidal state, does not necessarily signify anything regarding an analogous effect and a prevention of coagulation in other hydrosols [Compare, H. M. CASSELL, *J. Phys. Chem.* **42**, 955 (1938)]. Nevertheless, the gold number is of considerable interest in analytical chemistry, since it is a useful characteristic of organic protective colloids. The purity of protein preparations can be tested with its aid, and, likewise, changes in such materials (*e.g.*, in pathological processes) can be established. As yet, chemical methods are not available for such tests.

[87] C. PAAL, *Ber.* **35**, 2195 (1902).

a possibility that has scarcely been considered, namely, the planned production of protective colloids by preparative methods. The close relationships of, and the transitions between, complex formation, colloidizing, supersaturation, and hydrotropic solubilization, make it entirely probable that the introduction of certain atomic groupings may favorably influence not only the efficacy but also the selectivity of synthetic protective colloids. The studies of Traube and his collaborators[88] are of much interest in this connection. They found that the water-soluble potassium salt of cellulose sulfuric ester, $C_6H_7O_5(SO_3K)_3$, which is fairly easy to obtain, is an excellent protective colloid for metals and metal sulfides. Its protective action is also displayed in the prevention of the precipitation of $BaSO_4$, Ag_2CrO_4, and Hg_2CrO_4 below certain concentration limits. The great effectiveness of this synthetic protective colloid is shown, for instance, by the fact that no precipitate is formed on adding barium chloride to 10 ml. of $N/25$ sulfuric acid (containing 1 ml. of concentrated HCl) if 0.1 g. of this potassium salt is present. A further example of a synthetic protective colloid is dicresylmethanedisulfonic acid, whose presence prevents the precipitation of barium sulfate from acidified solutions.[89]

It is beyond the scope of this book to list the instances of protective colloid actions that are utilized for photometric determinations.[90] On the other hand, examples should be given here to illustrate the relationships and prospects with respect to the relevant questions of unequivocality and sensitivity of reactions. The first point to be stressed is the possibility that some organic compounds may function both as reagents and as protective colloids for their own reaction products. There is the further possibility that a reaction may produce materials that can serve as protective colloids. Instances of such simultaneous or dual reaction and protective effect are found in the reduction of noble metal salt solutions by tannin. The resulting finely divided metal is kept in colloidal dispersion by the colloidal tannin. Tests for noble metals are based on this effect. Conversely, a very sensitive test for tannin by means of dilute gold chloride solution[91] depends on the formation of a gold hydrosol, which is then protected by tannin (or its oxidation product). Ammonia likewise can be detected and determined colorimetrically (up to 0.01 mg./10 ml.) by adding tannin and silver nitrate

[88] W. Traube, B. Blaser, and K. Grunert, *Ber.* **61**, 755 (1928).

[89] Findings of H. Gerngross cited by W. Traube, *loc. cit.*, p. 767.

[90] In this connection, the following books are recommended: J. H. Yoe, Photometric Chemical Analysis, New York, 1938; F. D. Snell and C. T. Snell, Colorimetric Methods of Analysis, 2nd ed., New York, 1936; E. B. Sandell, Colorimetric Determination of Traces of Metals, Interscience, New York, 1944.

[91] A. Seyda, *Chem. Ztg.* **22**, 1052 (1898).

to the aqueous solution of ammonia. Colloidal metallic silver is produced.[92] The dispersion is bright yellow, orange, or red-orange depending on the quantity of ammonia. Here again the tannin acts as reductant and then as protective colloid. The following examples illustrate the formation of protective colloids during the course of chemical reactions. Pyrogallol or pyrocatechol are oxidized by gold salts to colored oxidation products, which then act as protective colloids for the colloidal gold produced at the same time. Sensitive tests for gold are based on this behavior. An excellent test for free sulfuric acid depends on the carbonization of sugar or cellulose. This is not solely a dehydration by the concentrated sulfuric acid resulting in the production of free carbon, but a redox process, as evidenced by the evolution of sulfur dioxide, also occurs. Higher hydrocarbons and acid oxidation products are probably formed,[93] and they exert a protective colloid effect on the finely divided carbon. It has been proved that colloidal monobasic acids are formed when carbon is oxidized.[94] The production of such colloidal oxidation products may also play a part in the determination of carbon in steel by the Eggertz method.[95] In this procedure, the steel is dissolved in nitric acid, and the color of the resulting solution, which contains particles of colloidal carbon and colloidal iron carbide, is compared with standards in a colorimeter. There is a possibility that the finely divided carbon is attacked by the nitric acid.[96]

The number of instances of the concurrent action of organic compounds as reactant and protective colloid, and of the action of reaction products of organic compounds as protective colloids, is still small. As has been pointed out, these instances have been observed exclusively in redox reactions. However, there is reason to suppose that further examples will come to light in the reactions of polyatomic organic compounds, especially among colloidally dispersed dyes. Possibly, many hitherto unexplained color reactions of biological materials, such as albumin, sugars, etc., belong in this category.

If the flocculation of colloidally dispersed particles by electrolytes is regarded as a chemical process, then the prevention of flocculation through the action of protective colloids becomes a reaction masking (see Chapter IV). The sensitivity of a qualitative test that is based on the production of a colored, insoluble material is not impaired by keeping

[92] K. G. MAKRIS, Z. anal. Chem. 81, 212 (1930); 84, 241 (1931).

[93] Compare L. SABBATINI, Kolloid-Z. 14, 29 (1914); S. TSCHUMANOV, ibid. 14, 321 (1914).

[94] K. A. HOFMANN and W. FREYER, Ber. 53, 2078 (1920).

[95] Compare W. W. SCOTT, Standard Methods of Chemical Analysis, Vol. 1, p. 232. New York, 1939.

[96] Compare J. H. WHITELEY, Iron and Steel, Carnegie Memorial 1917, 1.

the product in the colloidal condition, *i.e.*, by stabilizing the hydrosol condition, provided no misleading color changes result. Colloidizing is even an advantage in some cases because small amounts of a colored material are more visible when colloidally dispersed than if present in coarse aggregates. Conversely, the colloidizing of colorless or light-colored materials or reaction products, if it does not result in a distinct opalescence, is outwardly equivalent to loss of reactivity. The protective colloid action of cellulose sulfuric acid esters in the precipitation of barium sulfate, and also the earlier observation that this precipitation is hindered in alkaline casein solutions,[97] are examples of colloidal masking in precipitation reactions. A further instance is the prevention of a visible separation of calcium silicate, silver chloride and chromate in concentrated sugar solutions.[98] Another example was observed by Traube,[99] who found that potassium perchlorate cannot be precipitated by adding perchloric acid to a water solution of the potassium salt of cellulose sulfuric acid ester. Obviously, the potassium perchlorate in the colloidal state is protected by the cellulose sulfuric acid liberated in the reaction, or by its excess colloidal potassium salt. The result is a colloidal masking. In general, protective colloids are used to produce colored hydrosols when colorimetric determinations are to be made. Doubtless, this is the reason why the literature of analytical chemistry contains few statements concerning other effects of these materials, or so little regarding undesirable maskings of precipitations by protective colloids. However, empirical studies along this latter line have been made. For instance, it is a well known rule that products which contain organic materials should always be ignited or subjected to a wet oxidation before carrying out an inorganic analysis. The purpose of this preliminary treatment is to destroy completely the organic constituents and thus avoid any subsequent complex or colloidal masking by organic compounds. The presence of protective colloids can also alter the normal reaction picture of precipitation reactions that are being applied in organic analyses. For instance, the presence of albumin (or other protective colloids) interferes with the determination of sugar in urine by the Fehling reaction. The cuprous oxide then is apt to form a yellow sol and, if some of the copper remains unreduced, a green turbidity is obtained instead of the usual red precipitate. For this reason, any albumin should be removed from the sample, by boiling and filtering the urine before testing it for sugar.

Colloidal masking produced by protective colloids is not restricted to

[97] E. Feilmann, *Chem. News* **98**, 310 (1908).

[98] L. de Bruyn, *Ber.* **35**, 3079 (1902).

[99] W. Traube, *loc. cit.*, p. 481.

precipitation reactions. It has been found[100] that the enormous catalytic action of platinum hydrosol in the decomposition of hydrogen peroxide is reduced to about $\frac{1}{10}$ its value by the addition of gelatin, which probably coats the particles of platinum and thus lowers their activity. Other protective colloids likewise decrease the catalytic effect of colloidally dispersed platinum. As the influence differs from material to material, it is possible in this manner to differentiate colloidal proteolytic products.[101] In this connection, it may be pointed out that if a mixture of $CaCO_3$ and $Ca_3(PO_4)_2$ is dispersed in a gelatin gel, the carbonate is no longer preferentially dissolved by acids.[102] This observation indicates that care should be exercised when analyzing biological materials that may contain protective colloids. The "protein error" in acid-base titrations may be viewed as a colloidal masking that has general practical analytical significance. Sørensen[103] was the first to show that proteins and their decomposition products often interfere with colorimetric pH determinations. In the presence of these colloidal materials, the values are higher than those obtained by potentiometric methods. This influence of proteins is due to their ability to form soluble adsorption compounds, and the extent of the error depends on the indicator involved. The simpler the structure of the indicator, the smaller the protein error.[104] It has also been found[105] that, if gelatin is present, dilute red solutions of the alkali salts of Congo red and benzopurpurin, which are typical semicolloids, do not undergo the usual change to blue on the addition of acids. Likewise, mineral acids do not precipitate the blue dye from concentrated solutions containing gelatin, but, instead, brown sols of the colloidally dispersed dye acids result. These interesting cases of colloidal masking both of color reactions and precipitations are dependent on the concentration of the semicolloid. Aside from constitutional factors and the amphoteric character of proteins, the errors caused by them are primarily due to their colloidal nature. This concept is in agreement with the fact that the transition intervals of indicators are likewise displaced in soap solutions.[106] Aqueous dispersions of this semicolloid contain colloidal particles of fatty acids or polyions (see p. 454) produced by hydrolysis. These dispersed particles take over the adsorptive binding of the indicator and mask its normal color change. The findings with

[100] J. Gróh, Z. physik. Chem. **88**, 414 (1914).
[101] Compare T. Iredale, J. Chem. Soc. **119**, 109 (1921).
[102] R. E. Liesegang, Kolloidchemie, 2nd ed. p. 119. Dresden, 1926.
[103] S. P. L. Sørensen, Biochem. Z. **21**, 131 (1909).
[104] Compare A. Gutbier and H. Brinzinger, Kolloid-Z. **41**, 1 (1927).
[105] J. Alexander, J. Soc. Chem. Ind. (London) **30**, 517 (1911).
[106] A. Jarisch, Biochem. Z. **134**, 177 (1922).

Congo red and benzopurpurin support the view[107] that protective colloids are an especially important consideration when dealing with colored compounds of high molecular weight. Such colloids may bring about not only a lightening but also a deepening of the color. For example, if alkaline solutions of hematin contain gelatin or other protective colloids, the color is more intense than that of a solution of equal concentration but containing no protective colloid. The color of alizarin red in alkaline solution is reduced by small amounts of gelatin, and deepened by large quantities. It is obvious that such factors can play a part in qualitative color reactions and in colorimetric determinations.[108] The possible analytical utilization of anomalies in color reactions carried out in the presence of protective colloids has received practically no attention. However, the following case demonstrates that such application is fundamentally possible. The blue aqueous solution of the potassium salt of tetrabromophenolphthalein ethyl ester becomes yellow on the addition of dilute acetic acid. The blue can be restored by adding alkali. Consequently, such solutions behave like dyestuff indicators. If, however, a solution or suspension of native albumin is added to the dilute blue solution, a great deal of acetic acid can be introduced without causing the blue $\rightarrow$ yellow change. Only concentrated acetic acid, or mineral acids, are capable of breaking the bond between the protein and the ester or to cause the color change (rearrangement) of the ester adsorbed on the protein. This protein error was made the basis of a sensitive and selective test for native albumin, since its degradation products do not bring about colloidal masking.[109]

Although the electrolyte coagulation of suspensoids can be prevented by adding sufficient amounts of certain protective colloids, small amounts of the latter have the reverse result; they facilitate the flocculation. This interesting effect is called sensitization. Billitzer[110] was the first to study pure hydrosols from this standpoint. A large fund of experimental find-

[107] H. Wu and D. Y. Wu, in Alexander, Colloid Chemistry, Vol. 1, p. 380. New York, 1926.

[108] In this connection, it should be remembered that in unprotected, as well as in protected hydrosols, the size of the colored colloid particles determines, in large measure, the shade of the particular hydrosol. Consequently, hydrosols containing the same quantity of material but prepared under different conditions are not necessarily of the same color. This is why the test and standard solutions, that are to be compared in accurate colorimetric determinations, must be prepared under conditions that are as nearly alike as possible. It is especially important to maintain identical experimental conditions in nephelometric determinations, where not the color, but the degree of turbidity of suspended particles is compared in the presence of protective colloids.

[109] F. Feigl and V. Anger, *Mikrochim. Acta* **2**, 107 (1937).

[110] J. Billitzer, *Z. physik. Chem.* **51**, 145 (1905).

ings and literature on this subject is now available.   Sensitization is often explained by assuming that the sensitizing colloid itself is charged. Accordingly, its ions are adsorbed by the particles of the hydrophobic colloid, whose potential is thus lowered to the neighborhood of its critical flocculation value.[111]   This concept is in harmony with the fact that hydrophilic colloids may also actually coagulate hydrophobic systems.[112] However, as in the case of protective effects, the sensitizing action of hydrophilic colloids is not restricted to pure suspensoid hydrosols, whose formation has been completed, but extends into the hydrosol stage of a precipitation reaction.   Nevertheless, protective action and sensitization in pure colloidal systems are by no means identical with these same effects when encountered in analytical operations.   It has already been pointed out that an influence on the precolloidal stage of the formation of a precipitate must also be taken into account in protective action.   In sensitization, an additional effect on the particles of the precipitate in the colloidal range, both during and after coagulation, seems to be possible. Long before sensitization was recognized as a colloidal chemical phenomenon, Schulze[113] found that barium sulfate can be filtered and washed much more readily if a little gelatin is added to the suspension.   Likewise, suspensions of clay settle rapidly when treated in this way.[114] Caldwell and Moyer[115] have made interesting uses of sensitization in precipitation analyses.   They found that zinc sulfide (ca. 0.3 g.) can be obtained in a well coagulating, easily filterable form, if the weakly acidified solution (about 300 ml.) is treated with 0.5–2 mg. of gelatin, or 2–5 mg. of agar agar, either before or after passing in the hydrogen sulfide.   This expedient not only improves the condition of the zinc sulfide precipitate, but it also prevents the coprecipitation of small amounts of FeS, MnS, CoS, or NiS, which otherwise cannot be avoided.   Calcium fluoride normally comes down as a gelatinous mass, but a precipitate that filters easily is obtained from neutral fluoride solutions if 15 ml. of 10% gelatin is added.[116]   Wepritzkaja[117] advised the addition of gelatin when precipitating hydrated silica.   Weiss and Sieger,[118] who studied this recommendation thoroughly, found that 0.1 g. of gelatin (in freshly prepared solution) is enough to cause as much as 2 g. of SiO_2 to come down in an

[111] H. B. WEISER, J. Phys. Chem. 28, 1253 (1924).

[112] Compare, however, footnote 121 on p. 487.

[113] H. SCHULZE, Ann. Physik 129, 369 (1866).

[114] E. E. FREE [Eng. Mining J. 101, 509 (1916)] found that the addition of glue, gelatin, or soap favors the sedimentation of certain powdered minerals.

[115] J. R. CALDWELL and H. V. MOYER, J. Am. Chem. Soc. 57, 2372 (1935).

[116] N. F. MICHAILOWA, Chem. Abstracts 32, 1209 (1938).

[117] W. WEPRITZKAJA, abstract in Z. anal. Chem. 111, 287 (1937–38).

[118] L. WEISS and H. SIEGER, Z. anal. Chem. 119, 245 (1940).

easily filterable form. The alkali silicate solution, containing much hydrochloric acid, must be kept boiling during the gelatin treatment. Most of the silica is thus flocculated by the acid; the gelatin completes the precipitation and improves the condition of·the precipitate. This procedure can be used instead of the familiar tedious practice of acidifying the silicate solution, evaporating to dryness, baking the residue, filtering, and then repeating the evaporation of the filtrate. It is remarkable, that the gelatin can be replaced here by vegetable albumin, but not by egg albumin, gum arabic, or agar agar. Furthermore, other acids, at the same pH, have a lesser action than hydrochloric acid. Tungstic acid, WO_3, can be precipitated from solutions of alkali tungstates in this same manner; about 0.1 g. gelatin is required for 0.1 g. WO_3. Relatively small amounts of gelatin bring about the quantitative precipitation of niobic acid, zirconium phosphate, or tantalic acid from strongly acidified solutions. If excess barium chloride is added to a sulfate solution that has been acidified with hydrochloric acid, the fine suspension of barium sulfate is quite stable and filters poorly. This condition is easily overcome by a dropwise addition of agar agar solution to the suspension.[119] About 1 mg. of agar agar should be used per 0.1 g. $BaSO_4$. The precipitate settles rapidly and assumes the appearance of precipitated silver chloride. Unfortunately, it does not lose its ability to carry down potassium from solutions that contain potassium nitrate.

The preceding examples point the way to further uses of gelatin, agar agar, and perhaps other protective colloids as flocculating agents, and such possibilities should certainly be explored.[120] There is some question as to whether this effect is really a sensitization of an already existing coagulability. It is entirely possible·that insoluble adsorption compounds are formed as the result of the mutual action of particles in the colloidal range. This latter view is supported by the fact that all known cases indicate that sensitization is not a general characteristic of hydrophilic colloids but, like their protective action, it is selective. Compound formation of some sort is also indicated by the absence of gelatin in the filtrate from the zinc sulfide brought down in the presence of this sensitizing material. Coprecipitation of considerable quantities of gelatin is also observed in the procedure described by Weiss and Sieger (*loc. cit.*) in which the main bulk of the precipitate has already passed through the hydrosol condition.[121]

[119] E. J. BOGAN and H. V. MOYER, *Ind. Eng. Chem., Anal. Ed.* **14**, 849 (1942).

[120] W. WINDISCH and V. BERMANN [*Wochschr. Brau.* **37**, 130 (1920)] found that organic hydrophilic colloids can be distinguished by their divergent behavior in the sensitization of a ferric oxide hydrosol flocculation. Compare also J. REITSTÖTTER, *Z. Immunitätsforsch.* **30**, 768 (1921).

[121] Instances are known of sensitization of pure colloid systems in which there is no

Sometimes, sensitization of an electrolyte precipitation of suspensoid hydrosols can be achieved by organic nonelectrolytes that exert no protective colloid action. In this case also, the first observations were made on pure colloidal systems.[122] Studies by Caldwell and Moyer showed that this type of sensitization can be used in analytical procedures. They also demonstrated the important point that sensitization not only improves the form of a precipitate, but that sensitizing is connected with a deactivation of the surface of the particles. In other words, undesirable fixation of foreign materials may be decreased or prevented. This discovery opens up entirely new possibilities of diminishing or avoiding coprecipitations and induced precipitations, which are common sources of significant errors in precipitation reactions. The following findings will serve as examples. (a) If an acidified cupric solution containing zinc is treated with a little crotonaldehyde before hydrogen sulfide is passed in, the quantity of coprecipitated zinc sulfide is greatly diminished.[123] (b) Certain aldehydes, especially acrolein, prevent the contamination of zinc sulfide by cobalt sulfide, when the former is precipitated by hydrogen sulfide from weakly acidified solution.[124] This instance of the prevention of coprecipitation is particularly useful because the older methods require several reprecipitations of zinc sulfide to secure a complete separation of cobalt and zinc. (c) The end-point in the iodometric determination of copper is indistinct because the blue iodine-starch complex is carried down or occluded by the cuprous iodide. The addition of 0.5–1 ml. of 4% solution of white shellac in alcohol causes the cuprous iodide to settle out in heavy curds and without adsorption of iodine-starch.[125] Consequently, the released iodine can be sharply titrated with thiosulfate. (d) Nitrobenzene can be advantageously employed in the Volhard method for chlorides.[126] If nitrobenzene is present, the silver chloride is not contaminated with silver nitrate and

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difference in the charge of the particles. This shows that a sensitization does not invariably involve a flocculation of oppositely charged colloidal particles. Compare G. H. FISCHER and A. FODOR, *Kolloid-Z.* **32**, 279 (1923); G. A. BROSSA, *ibid.* **32**, 107 (1923); H. R. KRUYT, *ibid.* **31**, 338 (1922).

[122] H. BILLITZER, *Z. physik. Chem.* **45**, 312 (1903); H. FREUNDLICH and P. RONA, *Biochem. Z.* **81**, 87 (1917); P. KLEIN, *Kolloid-Z.* **29**, 247 (1921).

[123] J. R. CALDWELL and H. V. MOYER, *J. Am. Chem. Soc.* **59**, 90 (1937).

[124] J. R. CALDWELL and H. V. MOYER, *J. Am. Chem. Soc.* **57**, 2375 (1935).

[125] J. R. CALDWELL and H. V. MOYER, *J. Am. Chem. Soc.* **57**, 96 (1935).

[126] J. R. CALDWELL and H. V. MOYER, *Ind. Eng. Chem., Anal. Ed.* **7**, 38 (1935). E. ALEFELD [*Z. anal. Chem.* **48**, 79 (1909)] had previously reported that the addition of some ether to a silver halide precipitate so promotes its aggregation that the usual precipitation at elevated temperatures and subsequent digestion become unnecessary. He also stated that an analogous effect is secured by adding ether to other suspended precipitates.

the solubility is lowered enough to permit the titration of the excess silver nitrate with thiocyanate in the presence of suspended silver chloride. The necessity of filtering off the silver chloride is eliminated. The end-point of the titration is very sharp, since the precipitate is not colored and coagulates well. Obviously, this action involves the adsorption of extremely small amounts of the almost insoluble nitrobenzene on the surface of the silver chloride. This explanation is supported by the fact that the photo-sensitivity of silver chloride is greatly lessened if the chloride has been precipitated in the presence of nitrobenzene.

The preceding fact that traces of nitrobenzene are adsorbed on the surface of silver chloride particles and bring about aggregation of the substrate makes it very probable that the analytical flotation of finely divided precipitates (see p. 442) can also be regarded as a sensitized flocculation. When a fine suspension is shaken out with an organic liquid, which is not miscible with water, there is the possibility that small amounts of the organic liquid will be adsorbed on the surface of the particles. This will not only facilitate their aggregation, but also alter the surface in such a way that it becomes less hydrophilic because of the adsorption layer. The accumulation in the interfacial boundary between two immiscible liquids is thus brought about. A relevant example is colloidal molybdenum blue produced by the action of benzidine hydro-chloride and alkali acetate on silicomolybdic acid. The particles collect at the interface when the reaction mixture is shaken with amyl alcohol. This accumulation becomes an integral step in a sensitive test for silica in rocks, provided P_2O_5 is absent.[127]

Another effect is sometimes observed when hydrosols are shaken with organic solvents: the colloidal particles may enter the organic layer. The few recorded cases have mostly been in connection with analytical pro-cedures.[128] Wöhler[129] was the first to point out that the product of the $PtCl_4$-$SnCl_2$ reaction; namely, platinum-stannic oxide purple (see p. 471) can be extracted with ether or ethyl acetate. He used this effect in a sensitive test for platinum (0.1γ Pt/ml.). The analogous palladium and iridium purples are also soluble in these organic liquids. Denigès[130] found that ether extracts the colloidal molybdenum blue obtained by reducing acidified molybdate solutions with excess stannous chloride in

[127] F. FEIGL and H. LEITMEIER, Z. Krist. **40**, 1 (1929).

[128] The only statement besides that of L. Wöhler (Ref. 115) that could be found in the colloid literature is that of L. W. MILLER and R. H. McPHERSON, J. Phys. Chem. **12**, 706 (1908). They found that an As_2S_3 hydrosol can be partially extracted by shaking with ether.

[129] L. WÖHLER, Chem. Ztg. **37**, 938 (1907). Compare also L. WÖHLER and A. SPENGEL, Kolloid-Z. **7**, 243 (1907).

[130] G. DENIGÈS, Compt. rend. **171**, 802 (1920).

the presence of phosphate or arsenate.   He developed sensitive tests for phosphate and tin on the basis of this observation.   Hein and his coworkers[131] state that lower mixed oxides of the composition Mo_4O_{11} ($= Mo_2O_5 \cdot 2MoO_3$) are produced when heteropolyacids of molybdenum are reduced.   It is very likely that this oxide of quinquevalent molybdenum is stabilized if P_2O_5 or As_2O_5 is present, and thus prevent further reduction to lower (brown) oxides of molybdenum which are not taken up by ether.[132]

Feigl and Neuber[133] showed that the molybdenum blue formed by the action of stannous chloride on solutions containing phosphate, can be removed from the aqueous layer by extracting with amyl alcohol.   As little as 2γ P_2O_5 in 5 ml. (corresponding to a dilution of 1:2,500,000) can be detected in this way.   Bermann and Kulp[134] developed this qualitative test into a quantitative colorimetric procedure for the determination of extremely small amounts of phosphate.   This method was used to obtain interesting insights into the phosphate exchange occurring during alcoholic fermentation.   Molybdenum blue, which can be extracted by amyl alcohol, is produced by the action of carbon monoxide on solutions of palladium salts containing phosphomolybdic acid.   [The carbon monoxide is activated on the surface of the finely divided palladium produced by the reaction (see p. 140).]   The test for palladium based on this procedure has a concentration sensitivity of 1:40,000,000.[135] Strafford[136] used the amyl alcohol extraction of molybdenum blue produced from phosphomolybdic acid and stannous chloride in the colorimetric determination of small amounts of tin.[137]   Although the chemis-

[131] F. HEIN and coworkers, *Kolloid-Z.* **74**, 35 (1936).

[132] The natural assumption that the presence of colloidal stannic acid may play a part here, as in the solubility of platinum purple, is not warranted.   Many reducing agents other than $SnCl_2$ react with phosphomolybdic acid to form molybdenum blue which is soluble in ether.

[133] F. FEIGL and F. NEUBER, *Z. anal. Chem.* **62**, 369 (1923).

[134] V. BERMANN and E. KULP, *Wochschr. Brau.* **42**, 39 (1925); see also V. BERMANN, *Am. Brewer* **78**, No. 4 (1945).

[135] F. FEIGL and P. KRUMHOLZ, *Ber.* **63**, 1917 (1930).

[136] N. STRAFFORD, *Mikrochim. Acta* **2**, 306 (1937).

[137] Probably other applications will be found of the amyl alcohol extraction of colloidal molybdenum blue from heteropolyacids of molybdenum, and of the colorimetric determination developed by Bermann (footnote 134) based on this extraction. Phosphomolybdic acid is an excellent reagent for inorganic and organic reducing agents.   Since a slight blue is quite difficult to see in colored solutions, without comparison with a blank, extraction with amyl alcohol may enhance both the sensitivity and certainty of reducing tests in colored solutions, and even make quantitative determinations possible.   It should be noted that phosphomolybdic acid when dissolved in amyl alcohol gives yellow solutions.

try of the test for osmium, described by Wöhler and Metz,[138] has not been elucidated, it probably can be viewed as a colloid extraction. In this procedure trithiocarbonate is allowed to act on osmium solutions containing much hydrochloric acid. The olive-green product is soluble in ether. This test will reveal 10γ osmium.

A good example of the use of a combination of flocculation and extraction for the differentiation of the components of a hydrosol mixture is due to John and Beyers.[139] They make use of the ether-solubility of platinum, palladium, and iridium purples, and the corresponding insolubility of gold purple. The solution of the noble metals in aqua regia is treated with stannous chloride; a mixture of the colloidal purples results. The sol is shaken with half its volume of ether, and the gold purple remains as a foam in the ether-water interface. The other colloidal purples pass into the ether layer. Platinum purple is orange, palladium purple is red-brown, and iridium purple is yellow-brown. Since the gold purple no longer conceals the other colors, the appearance of the ether layer will give information concerning the kind and quantity of the platinum metals present.

It appears that the shaking of fresh precipitates with organic liquids may result not only in a flotation but, at times, also in the production of more or less stable suspensions in the organic liquid. Nickel dimethylglyoximate provides a good example of this effect. If a very dilute ammoniacal nickel solution (*circa* 1:1,000,000) is treated with dimethylglyoxime, the solution turns pale pink at first, and on standing red flocks of Ni-dimethylglyoximate separate. If, however, the mixture is shaken with ether or chloroform immediately after the reagent is added, a pink border forms at the ether-water-interface. If chloroform is used, it turns yellow because Ni-dimethylglyoximate is slightly soluble in this liquid, producing a yellow solution. With more concentrated nickel solutions, the flotation effect with ether is as before, whereas, in contrast, no yellow chloroform solution is formed, but the chloroform layer appears red throughout. Several hours later, the layers separate and the yellow solution then becomes visible. If the red chloroform layer is filtered through a dry paper, red Ni-dimethylglyoximate remains on the filter, and the filtrate is yellow. Obviously, a stable emulsion of Ni-dimethylglyoximate in chloroform is produced on shaking, and it gives the impression that the inner complex salt has dissolved in chloroform with a red color. It is probable that the very rare extractability of particles of an hydrosol depends on the formation of organosols. The particular con-

[138] L. WÖHLER and L. METZ, *Z. anorg. allgem. Chem.* **138**, 368 (1924).
[139] W. JOHN and E. BEYERS, *J. Chem. Met. Mining Soc. S. Africa* **33**, 26 (1932); *Chem. Abstracts* **27**, 39 (1933).

ditions necessary for this are not known.   In any event, not only analytical flotation, but also the possible extraction of colloidally dispersed particles by organic liquids should be given due consideration, because the sensitivity and, at times, the certainty of tests can be increased by this expedient.

ADSORPTION AS A GENERAL PHENOMENON OF THE ACCUMULATION OF MATERIALS ON SURFACES

Chapters IV and V, and also previous sections of this chapter, contain frequent references to adsorption, but with no attempt at defining this term.   Actually, its definition is quite difficult because adsorption phenomena cover such a wide range both as to type and intensity.   The deeper one studies the mechanism of adsorption processes with the hope of searching out the source and type of the necessary energy involved in these effects, the more apparent it becomes that a sharp division between adsorption and other physical or chemical processes is difficult to set up, in fact it is often impossible to do so.   It is much simpler to characterize the result of an adsorption.   This can be stated to be the more or less firm binding of a material at the boundary or, more correctly, in the interfacial area that lies between two phases.   Accordingly, adsorption is a process that invariably is closely related to the surface of a phase.

Adsorption always results in the concentration of a substance on the surface of a second material.   The substance on whose surface the accumulation occurs is called the adsorbent.   The term adsorbate is sometimes used to designate the adsorbent plus the material adsorbed on it.   Unfortunately, there is no English term for the material being adsorbed.   Since every adsorption requires the presence of a surface, liquids as well as solids can function as adsorbents.   Consequently, the following types of adsorption are theoretically possible:

Adsorbent	Adsorbed material
Liquid	Gas
Liquid	Liquid
Liquid	Solid
Solid	Gas
Solid	Liquid
Solid	Solid

In this tabulation, the state of aggregation of the adsorbed material is that which it had prior to the adsorption.   The question will not be debated here as to whether it is justifiable to speak of the aggregation condition of the adsorbed material when it constitutes a part of the adsorbate.

When dealing with the phase interfaces: solid-liquid, solid-solid, and

liquid-liquid, it is often purely a matter of viewpoint as to which is regarded as the adsorbent or as the material being adsorbed.   Generally, the material present in the smaller absolute quantity is taken to be the one that is being adsorbed.   .

If the adsorption of gases on solid or liquid adsorbents is left out of account, the adsorption of liquids on solid adsorbents is of special analytical importance.   The same is true regarding the behavior of solid adsorbents toward materials that are really dissolved or colloidally dispersed in liquids.   Solvent as well as its solutes are always adsorbed concurrently from solutions.   The solvent may be adsorbed as such, or it may be taken up in the form of solvates of the dissolved material.   These two varieties of adsorption of a solvent can well proceed simultaneously.   When colloidal dispersions (especially suspensoids), in which the colloidal particles constitute a solid phase of their own, are taken up on a solid, the adsorption is identical with the usual solid-solid type.

The term "positive adsorption" is applied to those cases in which a dissolved material is taken up to a relatively greater extent than the particular solvent.   This signifies that account is being taken of the quantity relationship between solvent and solute, in other words, the relative values before and after adsorption.   "Negative adsorption" is the reverse process, namely, the relatively greater retention of a solvent as compared with the materials dissolved in it.   When dealing with the adsorption of dissolved materials, or of gases, on the surface of solid or liquid adsorbents, positive adsorption can be regarded as denoting an increase in the concentration of gases or dissolved materials on the boundary separating two adjacent phases.   It is difficult to establish this increase in concentration directly; and sometimes it is impossible. The difficulty arises from the fact that the adsorption layer is, as it were, a three-dimensional phase of extremely small depth, and, in the absence of a method of measuring the surface and the thickness, there is no way of learning the volume of the adsorbate corresponding to each concentration.   However, an indirect measure of the increase in concentration in the adsorption layer can be secured from the decrease in concentration in the original adsorption medium, i.e., in the space filled with the solution or gas prior to contact with the adsorbent.   The quantity of material held by a solid adsorbent can be brought into relationship with the quantity of the adsorbent or its surface.   The first ratio is easily determined.   On the other hand, the relation to the adsorbing surface can be established only in exceptional cases, since it is seldom possible to make an accurate measurement of the area of a solid surface, especially of powders or gel-like materials.   A further difficulty is introduced by the fact that not all parts of a free surface adsorb with equal intensity.   The

extent of adsorption on crystalline materials sometimes differs on the various surfaces. Corners and edges are preferred places. In addition, inhomogeneities can behave abnormally since adsorption on them may be greater or less than on neighboring areas.

Adsorption processes usually proceed with striking rapidity. They are concluded within a few minutes, or at least reach a point after which any additional adsorbing action is extremely slow. Just because of this rapidity it may be supposed that the adsorbed material is fixed on the surface of solid adsorbents and does not enter the interior. If the adsorbed material does not stay in the boundary layer, but migrates into the interior of the adsorbent and distributes itself there homogeneously, the process is called absorption. Accordingly, absorption is always preceded by an initial adsorption and the occurrence of absorption can be recognized by the fact that the taking up of a material is unusually retarded or, more correctly, that a period of rapid up-take is followed by one in which the process is slower. However, the slow stage of absorption is not necessarily due to an actual migration, i.e., a diffusion of the initial adsorption layer into the interior of a solid adsorbent. It may be no more than the outward manifestation of a slow filling of numerous fine capillaries of a solid following the covering of the outer surface. Obviously, the total process of taking up a liquid or a solution by a solid must depend to a great measure on the form-species of the latter. If the adsorbent consists of an assemblage of extremely thin lamellae, as found, for example, in gelatinous precipitates, there need not be more than a slight passage of a material from the surface into the interior to give, as a final effect, the picture of an absorption. McBain[140] introduced the term "sorption" to take care of such doubtful cases.

The extent of adsorption (sorption) of a dissolved material on the surface of a solid depends on a variety of factors. These include: (1) the chemical nature of the adsorbent and the material being adsorbed; (2) the structure of the adsorbent, including its form-species (crystalline or amorphous), the particle size (hence, the free surface), the nature of the surface (smooth or rough), content of inhomogeneities in the surface layer, etc.; (3) the ratio of the quantity of adsorbent to that of the material being adsorbed, and the concentration of the latter; (4) the degree of dispersion of the material to be adsorbed (in true or colloidal solution); (5) the nature of the solvent that contains the material to be adsorbed; (6) the cosolutes present in, and pH of, the solution; (7) temperature and pressure. Patently, this large number of factors, whose determining influence in some cases was readily recognized, may shape the picture of adsorption phenomena in so many ways that it is often hard to believe

[140] J. W. McBAIN, Z. physik. Chem. 68, 471 (1907).

that the varied types of adsorption have a common underlying principle. When, on the basis of analogous features, attempts are made to differentiate certain types of adsorption, it is possible almost at once to distinguish between reversible and irreversible adsorption.

The establishment of an equilibrium is the determining characteristic of the reversible adsorption of materials from solution. This signifies that at equilibrium there is, for each concentration of the solution, a definite relation between the quantity of the adsorbent and the quantity of material adsorbed. In other words, an adsorbate of a certain composition exists at each concentration. The relations involved in an adsorption equilibrium can be expressed by the empirical equation developed by Freundlich.[141] This "adsorption isotherm" is usually written:

$$\frac{x}{m} = ac^b$$

in which x = weight of adsorbed material

m = weight of adsorbent

c = concentration of solution at equilibrium

a and b = constants that depend on the nature of the adsorbent and adsorbed material. For many systems, b lies between 0.1 and 0.7

This relationship is valid with respect to a reproducibility of the values of x only when it is assumed that the particular adsorbent remains in the same condition with regard to its purity and surface distribution. For example, in measurements of adsorption on charcoal, it is not a matter of indifference which variety of this adsorbent is used (blood or wood charcoal, etc.). In comparative trials it is essential always to employ the same kind of charcoal, for instance (compare p. 510). It is consistent with the meaning of the term "adsorption equilibrium," that, on dilution or concentration of the adsorption system, the quantity of adsorbed material adjusts itself until it reaches the same value it would have attained had the adsorption occurred directly from the solution at the final lower or higher concentration. Therefore, a material that has been reversibly adsorbed can be completely removed from the adsorbent by washing with the pure solvent.

The course of an adsorption can be clearly shown by plotting its isotherm on a system of rectangular coordinates. The weights adsorbed per unit weight of adsorbent (x/m) are entered along the ordinate, and the equilibrium concentrations along the abscissa axis. A parabolic curve is obtained; at high concentrations it practically reaches a limiting

[141] H. FREUNDLICH, Colloid and Capillary Chemistry (tr. by H. Hatfield), p. 111 ff. London, 1928.

(saturation) value that is determined by a. This constant represents the fraction taken up by the adsorbent from a solution whose concentration is unity ($c = 1$), which, in terms of the usual units (molarity, normality, *etc.*), is a relatively high concentration. The constant b represents the slope of the rise from the null point on; in other words, the concentration range within which the major part of the saturation quantity is taken up. The shape of this curve shows that relatively more material is adsorbed at low concentrations, and this is more definitely the case the steeper the curve. It is characteristic of an adsorption process, that on gradual addition of the soluble material only a part of it is taken up by the solid phase while the rest remains in solution. This behavior is fundamentally distinct from that of a solid reacting with a dissolved material to produce a stoichiometrically defined solid compound which appears as a new phase. In the latter case, gradual addition of the soluble reactant results either in its complete consumption to form a compound at a constant equilibrium concentration, or the added material remains entirely in the solution after the solid has reacted completely. The graphic representation of this latter process accordingly does not give a parabolic curve but, instead, a diagram made up of horizontal and vertical straight lines. In case the solid forms a series of compounds with the soluble reactant, a step-like graph results.

Accordingly, adsorption can be plainly recognized only within a certain concentration range, namely, before saturation is reached. In the saturation range it is difficult to distinguish adsorption from a reaction in which a definite solid compound is formed by the interaction of a solid and a dissolved material. The steeper the adsorption isotherm, the lower the concentrations at which practical saturation is reached. In the limiting case, these concentrations ($b < 0.1$) may be so small that analytical detection can be extremely difficult or impossible. If the soluble material is gradually introduced into the solvent that is bathing the adsorbent, the first portions will then be taken up completely, so that no appreciable amount remains in solution. If such gradual addition is continued until saturation is finally reached, any further portions remain entirely in the solution. In such cases, introduction of the adsorbent into the solution can result in practically complete removal of the dissolved material. If attempts are then made to recover the adsorbed material by washing, such large volumes of solvent will be required that the process is not feasible. Under such circumstances the adsorption is "irreversible." The alternative term "chemosorption," which is sometimes used, seems quite apropos in view of the marked similarity of irreversible adsorption to a chemical reaction in which the adsorbent produces a new insoluble compound. Furthermore, such tenacious

binding must be the reflection of extremely strong reciprocal actions between the molecules of the adsorbent and the adsorbed material, as intense as those in principal valence compounds or very stable complex compounds. The weaker forces involved in reversible adsorption are more comparable with those that are active in the union of solvent and solute to form solvates. The available knowledge of the chemical characteristics of adsorbent and adsorbed material, together with observations of any accompanying color changes, *etc.*, are often adequate to reveal the type of union that has been effected. Nevertheless, it must still be said that the previously dissolved components are bound by the solid to form an adsorbate, since the binding parts of the adsorbent have remained in their original state of association with the portions that are more distant from the adsorbed molecules and have not been transformed into a new phase. The variability of the composition of the adsorbate with changing conditions surrounding the preparation of the adsorbent, the absence of a rational stoichiometric composition, the failure to exhibit new X-ray interferences, and still other factors, support the correctness of this viewpoint.

The foregoing discussion demonstrates that it is not possible to draw a strict line between reversible and irreversible adsorption. If the adsorption equilibrium greatly favors the adsorbate, *i.e.*, if the equilibrium concentration (c in the adsorption isotherm) is quite small, the decision as to whether unadsorbed portions remain in solution or whether an adsorbed material is parted from the adsorbent on washing with the pure solvent, is determined by the sensitivity of the particular method of detection employed. A trial with a less sensitive test may indicate irreversibility, which will not be substantiated by more exact methods. In passing, it is well to point out that neither absolute reversibility nor irreversibility can occur. Likewise, the designation chemosorption for irreversible adsorption is no longer a fortunate one, if adsorption is considered in the light of a chemical union as was first done in a general form by Haber and Langmuir. Haber[142] was the first to make the assumption that the atoms on the surface of the lattice of crystalline materials take over the binding of molecules of gases, liquids, and dissolved materials. The surface atoms of a crystal, in contrast to those in the interior, are not fully saturated in all directions, but only toward the interior and the sides. Consequently, there remain binding forces directed outward, which represent the field of adsorption. This supposition, whose kinship with the concepts of coordination chemistry is unmistakable, and according to which the reversible adsorption of materials is a kind of loose union,

142 F. HABER, *Z. Elektrochem.* **20**, 521 (1914).

was developed further by Langmuir.[143] Naturally, the Haber-Langmuir theory also applies to the residual valence action of atoms of amorphous substances. Increasing the irregularity (roughness) of solids thus will lead, not only to an increase in the specific surface available for adsorption, but also to an increase in the number of available residual valences. It is consistent with this theory to suppose that the depth of an adsorption layer cannot exceed the range of chemical binding forces, and accordingly it extends essentially to the thickness of one molecule.

Only the uppermost molecular layer of the adsorbent, and that of adsorbed material which is held there, need be considered as constituting the adsorption layer. The interior of the adsorbent remains unaltered. Hence, adsorption is a reaction that takes place on the surface only and limits itself to the surface. This localization is a necessary criterion for adsorption for the following reason. In many instances, the interaction of gaseous or liquid (dissolved) materials with a solid begins on its surface, and proceeds from there into the interior, so that eventually the entire solid may react. Although this type of reaction likewise occurs for the time being on a surface, it is not an adsorption because the reaction product is formed as a separate phase. On the other hand, a change, which can be formulated stoichiometrically, of molecules situated on a surface can be an adsorption if the reaction products remain in the phase domain of the solid reactant. Such continuance occurs when the molecules of a product are held by the surface molecules of the unchanged solid which undergoes no further change. There is, however, another possibility of the continuation of reaction products in phase association with a solid reactant, namely, if, through a chemical change, only certain portions (atomic groups or ions) are taken up by surface molecules, and the uncaptured portions do not leave the original molecular association (e.g., the lattice in the case of crystals). Therefore, the non-reacting interior of an adsorbent is an integral component of the system; it is linked with the adsorption layer, and, together with it, constitutes the adsorbate, which may have properties differing from those of its component parts. An important question concerns the stoichiometric relation of these components. In other words, what is the chemical significance of the term x/m in the adsorption isotherm? The concept advanced in the foregoing discussion leads to the expectation that there is a rational relation between the number of molecules of the adsorbent and adsorbed material that make up the adsorption layer, or of those parts of the surface on which adsorption has occurred. Of course there is no such rational relation with respect to the entire adsorbate, i.e.,

[143] I. LANGMUIR, *J. Am. Chem. Soc.* **38**, 2221 (1916) **39**, 1848 (1917); **40**, 1361 (1918).

unchanged adsorbent plus adsorption layer. Rather, in general, there is an enormous disproportion between the molecular numbers and, accordingly, also between the absolute quantities of adsorbent and adsorbed material. A rational relationship in the adsorption layer will be approached more closely the greater the specific surface. In fact, it is possible to conceive, as the extreme case, that practically the entire adsorbent is present as surface, and that a quantitative reaction, and consequently a rational stoichiometric composition, would thus be secured. In those instances in which the adsorbed material represents a considerable fraction of the adsorbate, it is common practice to speak of adsorption compounds (see p. 547). It must be kept in mind that, if a situation arises in which the entire body of the adsorbent reacts quantitatively, the case no longer belongs in the category of adsorption. The latter process is inherently associated with the existence of interfaces and, hence, rests fundamentally on the possibility of distinguishing between the surface of an adsorbent and its interior. Accordingly, if an adsorbent reacts *in toto*, the process is not an adsorption, even though it does not involve a transformation into a new type of phase.

The concept of the adsorption process as a surface reaction or, more correctly, as a reaction of the molecules or ions situated on the surface of a solid, makes it possible to classify adsorption phenomena according to the type of the resulting products, which usually are not stoichiometrically defined. A great class of adsorbates can be placed in parallel with the addition compounds, that are so common among complex compounds. The designation molecular adsorption or addition adsorption is quite appropriate for adsorbates of this kind. Weitz[144] made a discovery that is very interesting in this connection. He found that triarylmethane halides, tetraethyl hydrazines, and other substances which produce colored molecular compounds with acids and certain metal salts ($ZnCl_2$, $AlCl_3$, etc.) produce the colors of these molecular compounds when they are adsorbed on silica gel or alumina from benzene, chloroform, or carbon tetrachloride solutions. Furthermore, these molecular compounds, and also these adsorbates, are again decomposed, with discharge of the color, on treatment with the same solvents (alcohol, acetone, water, etc.). As shown by the preceding instances, the molecules of the adsorbed material in an addition adsorption can be displaced by other species of molecules. The displacing molecules may come from certain solvents or from materials dissolved in them. A solvent, from which an adsorption occurs, can itself take part in a displacement. This is demonstrated in reversible adsorption. It is frequently found that a

[144] E. Weitz, *Ber.* **72**, 1740, 2099 (1939); *Z. Elektrochem.* **26**, 222 (1940); **47**, 165 (1941).

material which is irreversibly adsorbed from its dilute solution in one solvent, can be dislodged from the adsorbate by another solvent, whose molecules are then adsorbed in turn. For example, it is well known that dyes that are irreversibly adsorbed on charcoal from water can often be displaced by washing with alcohol or other solvents. Frequently, this type of desorption can be applied to remove or detect traces of materials that adhere to an adsorbent. For instance, when an aqueous solution of night blue (or methylene blue) is shaken in a glass vessel, the solution poured off, and the vessel then rinsed until the washings are colorless, invisible traces of the dye still remain on the glass. If the container is now moistened with several drops of alcohol, a blue solution is obtained.[145] Hence, the alcohol displaces the traces of dye that were irreversibly adsorbed on the glass. It might also be said that the adsorption equilibrium: aqueous dye solution-glass is replaced by the adsorption equilibrium: alcoholic dye solution-glass. Since the latter equilibrium is less favorable to the adsorption of the dye, the latter is desorbed from the glass. The following experiment illustrates the desorption of a material from a solid surface by a second material dissolved in the same solvent from which the adsorption took place.[146] A dilute water solution of fuchsine is decolorized on shaking with charcoal because the dye is irreversibly adsorbed. If the charcoal is then digested with a solution of saponin, the latter is adsorbed and displaces the dye from the surface. As a result, the solution immediately regains its color.

It is consonant with the idea of addition adsorption that the molecules of the adsorbed material in the adsorbate must be oriented in a definite way with respect to the molecules on the surface of the adsorbent. This seems logical since the binding forces necessary to the occurrence of an adsorption have their seat in certain atoms of the adsorbent and adsorbed material. Addition adsorption brings molecules of these materials into immediate spatial relationship with each other. A possible result may be that an initial addition adsorption can be followed by condensation and exchange of place reactions between the respective molecular species. This possibility is not surprising if it is recalled that numerous examples are provided, in organic reactions, of the production of precompounds, which invariably are molecular compounds of the components. Sometimes, these precompounds can be isolated in the pure state, and the corresponding final products then produced from them by inner molecular reactions. It is obvious that the probability of isolating such precompounds increases with the rate of the addition reaction that is requisite for their formation and the slower the succeeding inner molec-

[145] Cited from E. S. HEDGES, Colloids, p. 131, London, 1931.
[146] Cited from E. S. HEDGES, op. cit. p. 133.

ular reaction. However, addition adsorptions, as a rule, proceed very rapidly, and in case a slow subsequent inner-molecular reaction leads to products of another type, the possibility will be provided of discerning the transformation through an accompanying color change. Bayliss,[147] in a study that has become one of the classics of colloidal chemistry, found an instance of this in the system: aluminum hydroxide-Congo red. If well-washed aluminum hydroxide (zirconium and thorium hydroxides behave similarly) is treated with small quantities of a dialyzed blue solution of Congo red, the Congo acid is adsorbed and the hydroxide precipitate is consequently colored blue. On standing, and especially on warming, the blue product turns red, because of the formation of an aluminum (zirconium or thorium) salt of Congo acid. A counterpart of the Bayliss experiment was provided by Thiele.[148] He studied the behavior of p-nitrobenzalamidoguanidine toward wool, i.e., an acidic adsorbent. On treatment with acids this basic nitro compound forms salts and the yellow aqueous solution becomes colorless. The action is reversed by the addition of alkalies, and the yellow dye-base is released. When the aqueous solution acts on wool, the latter adsorbs the dye and becomes yellow. The color disappears on warming because the adsorbed dye then forms a colorless salt with the acidic groups of the wool. If the colorless wool, freed of excess solution, is then spotted with ammonia, the color is restored because the yellow base is again liberated.

The foregoing instances demonstrate that the reaction of an adsorbed material with its adsorbent to form a salt can be seen directly if the change from adsorptive-binding to salt-binding is accompanied by a color change. However, such transformations can be made manifest by still other methods. It will be recalled that reversible adsorption leads very quickly to an equilibrium whose attainment and position are practically independent of temperature. A departure from this rule, i.e., if an initial reversible adsorption gradually (or more quickly on warming) leads to an irreversible binding, then a further chemical process probably has followed the chemical process of adsorption. An observation, reported by Lake[149] is a case in point. He found that at 20°C. wool takes up very little acid violet from an aqueous solution, whereas a great deal of the dye is bound at 95°C. Furthermore, the dye cannot be extracted from the wool by water at room temperature. A change in the type of union has obviously occurred; it is quite probable that the dye has formed a salt with the acidic groups of the wool.

Important studies on adsorption, initiation of salt-formation by

[147] W. M. BAYLISS, Proc. Roy. Soc. (London) 84, 81 (1911).
[148] J. THIELE, cited from E. WEDEKIND, Z. angew. Chem. 39, 740 (1926).
[149] D. B. LAKE, J. Phys. Chem. 20, 761 (1916).

adsorption, and superposition of these processes in the case of zirconium hydroxide were made by Wedekind and Wilke.[150]   This gel adsorbs large amounts of arsenious acid, arsenic acid, and phosphoric acid, reversibly at first, so that the adsorption equilibrium is established within a few minutes.   In the case of arsenious acid, the reversible adsorption persists; neither heating nor employment of excess arsenious acid leads to the production of arsenite.   In contrast, the adsorption of the other two acids gradually becomes irreversible, and a time reaction, that can be readily followed, produces a salt.   The maximum uptake of P_2O_5 corresponds to the compound $Zr(HPO_4)_2$.   This compound is also produced when PO_4^{---} ions react with an acidified solution containing Zr^{++++} ions.   The reaction of zirconium hydroxide with hydrogen peroxide to produce zirconium peroxide hydrate likewise proceeds through an addition adsorption.   These workers also found that aluminum hydroxide takes up phosphoric acid reversibly at first, but in this case the adsorption leads to the production of phosphate only after a long time (14 days boiling).   It may be concluded from the investigations of Wedekind and Wilke that the action of acids on solid bases does not necessarily lead immediately to a stoichiometric salt-formation, but that an adsorption stage, whose stability may be more or less long-lived, may intervene.

All the foregoing instances have involved adsorption between basic (or acidic) adsorbents and acidic (or basic) adsorbed materials.   The fact that adsorption is favored by polar contrasts between the materials that function, respectively, as adsorbent and adsorbed material is in entire harmony with the concept that adsorption is a chemical process. In fact, the findings of Bayliss are also limited to basic oxyhydrates. Despite their gel-like structure, acidic hydrous oxides, such as $SiO_2 \cdot aq$ or $SnO_2 \cdot aq$, are inactive toward Congo acid.   Accordingly, adsorption demands not merely a great development of surface, but, in addition, specific binding forces must be active in the surface.   Rheinboldt and Wedekind[151] studied the adsorption of acid and basic dyes on basic and acidic materials and thus provided much information concerning the relation of adsorption to polar contrasts between the adsorbent and the adsorbed material.   It is often stated that adsorption is the preliminary stage of chemical union.   This viewpoint is misleading if it implies that there is a deep-seated distinction between adsorption and compound formation.   Adsorption, *per se*, constitutes the production of compounds

[150] E. WEDEKIND and H. WILKE, *Kolloid-Z.* **34**, 83, 283 (1924); **35**, 23 (1924). Compare also compilation by E. WEDEKIND, *Z. angew. Chem.* **39**, 740 (1926).

[151] H. RHEINBOLDT and E. WEDEKIND, *Koll. Beih.* **17**, 115 (1923).   Compare also R. E. MARKER and N. E. GORDON, *Ind. Eng. Chem.* **16**, 1186 (1924); A. M. MORLEY and J. K. WOOD, *J. Soc. Dyers Colourists* **39**, 100 (1923).

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of varying stabilities. Actually, in those instances where salt-like compounds between adsorbent and adsorbed material are formed, place exchange or condensation reactions are involved in the transformation of an addition compound produced on the surface into a salt-like compound. This reaction product can either remain in the phase association of the adsorbent, or it may separate from the latter to produce a new phase. Adsorption is only involved in the first case, and then only when the transformation is incomplete. In the second case, namely, when a new phase is formed, an adsorption is an intermediate stage and the adsorption process is a partial reaction in the course of the total process of a direct reaction of solids with materials that are in true or colloidal solution. The role of adsorption as a partial reaction is quite apparent in the action of the hydrosol of Prussian blue on metal oxyhydrates and hydroxides. Wedekind and Fischer[152] found that $Mg(OH)_2$, $Al_2O_3 \cdot aq$, as well as the oxyhydrates of La, Th, Ce, Nd, Pr, Y, Gd, and Er adsorb colloidal Prussian blue particles rapidly and turn blue. However, the color disappears after a while, more rapidly on warming. Reaction occurs with production of $Fe(OH)_3$ and the corresponding ferrocyanides. In the case of $Mg(OH)_2$, this reaction can be discerned directly through the production of water-soluble $Mg_2Fe(CN)_6$. The colloidal Prussian blue does not tint $Zr(OH)_4$ or HgO; instead the blue color is slowly discharged. Hence, it might be concluded that no adsorption takes place in these instances. However, these materials are turned blue at 0°C. and the adsorption color disappears at room temperature. Since adsorption processes are only slightly dependent on the temperature, the cooling obviously slows down the chemical reaction that follows the adsorption. It proceeds too rapidly at room temperature to permit the adsorption stage to be seen. Neither adsorption nor chemical reaction is shown under any circumstances by the acidic oxides $TiO_2 \cdot aq$, $WO_3 \cdot aq$, $Ta_2O_5 \cdot aq$, nor by the basic $Pb(OH)_2$. These studies show definitely that basicity of the substrate is by no means the dominant factor in the adsorption and reaction of Prussian blue, because $Pb(OH)_2$ is indubitably more basic than the majority of the oxyhydrates tested. The great similarity of $Zr(OH)_4$ to $Th(OH)_4$ is not exhibited in their adsorption of Prussian blue, and basic $Pb(OH)_2$ behaves like the acidic substrates. Consequently, a factor is involved here which is important with respect to the topic under consideration, namely the occasional marked selectivity of an adsorption. This will be taken up later.

Among the types of adsorption, addition adsorption is worthy of particular attention here. It is encountered among many organic compounds, especially those of nonelectrolytic character. The extent of the

[152] E. WEDEKIND and J. FISCHER, *Ber.* **60**, 544 (1927).

adsorption, on a particular adsorbent, is determined both by the nature of the solvent and the solution state of the material that is being adsorbed.[153] It has been observed, for example, that iodine is adsorbed more extensively from its violet solutions in chloroform, benzene, *etc.*, than from its brown solutions in alcohol, ether, and so forth. The latter solutions contain solvates of iodine, *i.e.*, compounds of iodine with molecules of the solvent, whereas the iodine in violet solutions is in the same condition as when in the vapor state. In this connection, it is interesting to note the action of picric acid toward silk. Walker and Appleyard[154] found that this dye is reversibly adsorbed from aqueous solution, while it is not taken up at all from benzene solution. Accordingly, it might be expected that silk impregnated by bathing it in water solutions of picric acid and then dried, would readily yield the adsorbed material when extracted with benzene. This is not the case, however; the reversible adsorption of picric acid from water solution has become irreversible toward benzene. The reason for this anomaly is that picric acid is not in the same solution state in water and benzene. This is evidenced by the fact that aqueous solutions are quite yellow, while benzene solutions are practically colorless. When dissolved in water, picric acid probably is present, for the most part, as the hydrate of an isonitro *aci* form, whereas benzene solutions contain the isomeric phenol *aci* form (see p. 282). Obviously, silk adsorbs only the isonitro *aci* form to any considerable extent, and this form is so firmly held in the adsorbate that extraction of the dye with benzene is not possible. This is true despite the fact that both water and benzene solutions of picric acid must contain equilibrium mixtures of the two isomeric forms.

When addition adsorption of nonelectrolytes occurs from mixtures, both substances, as a rule, are adsorbed to a lesser extent than when they are present singly. Sometimes one of the dissolved materials is adsorbed preferentially. The selective adsorption of nonelectrolytes, especially those that are organic in nature, is more marked if, instead of adding an adsorbent to the solution of two or more materials, the solution is allowed to flow by the adsorbent, which is subsequently washed with the pure solvent. This procedure will be discussed in more detail in the section on adsorption analysis.

Before considering the behavior of strong electrolytes toward solid adsorbents, it seems desirable to note certain facts regarding the adsorption of colloidally dispersed materials. It should be remembered that colloid particles can be viewed as giant ions (see p. 451). In these

[153] Compare E. HEYMANN and E. BOYE, *Z. physik. Chem.* **150**, 219 (1930); E. HEYMANN, *Kolloid-Z.* **58**, 81 (1931).

[154] J. WALKER and J. R. APPLEYARD, *J. Chem. Soc.* **69**, 1334 (1896).

colloid ions neutral molecular aggregates acquire a stabilizing charge either from ions furnished by their dissociation or from adsorbed foreign ions. Accordingly, the adsorptive behavior of colloid ions can be expected to occupy a hybrid position, according to whether the ionic or the polymolecular component participates in the adsorption process. In the latter case, analogies to the previously discussed addition adsorption of molecules may be expected, and possibly to the subsequent secondary processes [see, for instance, the adsorption of Prussian blue sol on metal hydroxides (p. 503)]. The events accompanying the adsorption of ions will be discussed presently. It will suffice here to point out that Biltz,[154a] in his classic studies, showed that the adsorption of colloidally dispersed inorganic materials on solid adsorbents conforms to the adsorption isotherms in the same manner as when truly dissolved materials are adsorbed. Despite the analogy to the adsorption of materials from true solution, it may not be forgotten that colloidal particles, because of their dimensions, also occupy a special position. Frequently, a solid-solid adsorption is encountered in which there is doubt as to which of the participants is to be regarded as the adsorbent and which as the material being adsorbed. The adsorption process primarily affects only the surface portion of the participants, while the interior on both sides remains unaltered.

The adsorption of inorganic electrolytes is restricted almost entirely to aqueous solutions. Consequently, variability in the adsorption due to substitution of other solvents is eliminated. However, other complications arise because an aqueous solution of an electrolyte is by no means a solution of a single material. Undissociated molecules, at least two ionic species, and possibly soluble hydrolytic products are present. All of the ionic and molecular species that exist in the solution of an electrolyte may compete for fixation on an adsorbent. They behave, with respect to this goal, as though they were independent cosolutes, much like the individual effects they display in osmotic pressure and other related physical effects of a solution. If molecules of an electrolyte, i.e., anions and cations in equivalent amounts, are taken up, the adsorption is said to be apolar. This corresponds to the addition adsorption of non-electrolytes. However, the various ions of an electrolyte often exhibit different adsorption tendencies; in other words, non-equivalent quantities of the cations and anions are directly fixed on the surface of an adsorbent. This is known as polar adsorption.[155] Euler and his collaborators[156] have provided instances of apolar adsorption. They found

[154a] W. Biltz, Ber. 37, 1766 (1904); 38, 2969 (1905).
[155] L. Michaelis and P. Rona, Biochem. Z. 102, 268 (1922).
[156] H. v. Euler et al., Arch. Kemi, Mineral Geol. 7, 1 (1920); 8, 1 (1922).

that there is no preferential adsorption of cations or anions when silver nitrate or potassium chloride is taken up on the surface of finely divided metallic silver or gold.   The apolar adsorption of hydrochloric acid on ash-free charcoal is quite remarkable.   Miller[157] reported that 2.3 g. of charcoal adsorbs almost 0.3 millimole of HCl so strongly, that not even traces of the acid are released on washing with conductivity water at room temperature.   Only half of the adsorbed hydrochloric acid is set free even after 15 washings with boiling water.[158]   This tenacious binding probably explains why materials adsorbed on charcoal are so often easily displaced by hydrochloric acid.   For the same reason, neutral salts that normally hydrolyze little, if at all, may be extensively decomposed if their water solutions are placed in contact with ash-free carbon.   Miller and his associates,[159] by most careful studies, showed that only acid is adsorbed in such cases, while equivalent quantities of base remain in the solution.   For instance, sodium benzoate solutions deliver benzoic acid, which can subsequently be extracted from the carbon by organic solvents, the quantities thus obtained corresponding exactly to the base that remains in the water solution after the adsorption.   Obviously, the decomposition of neutral salts into acid and base by the intervention of water, can occur only if the carbon withdraws the acid derived from even an unfavorable hydrolysis equilibrium: $MeX + HOH \rightleftharpoons MeOH + HX$. Hence, this type of adsorption, which is likewise capable of shifting the hydrolysis equilibrium from insignificant proportions into the measurable range, is called hydrolytic or fission adsorption.[160]   Thus, an alkaline reaction results if a solution of NaCl or Na_2SO_4 is shaken with $Cu(OH)_2$, which preferentially adsorbs HCl or H_2SO_4.[161]   Fibrous alumina acts analogously toward various salts.[162]   If silica gel is placed in contact

[157] E. J. MILLER, *J. Phys. Chem.* **31**, 1197 (1917).

[158] This strong adsorption of acid readily explains why an acid rather than a pure charcoal is obtained by the procedure formerly used to purify this adsorbent.   In this, the charcoal was treated with HCl or aqua regia and then washed with water until the filtrate was no longer acid.   (Incidentally, this procedure does not remove silica.)   Such preparations can easily lead to erroneous results if employed in adsorption experiments.   Miller (*loc. cit.*) showed that the only method of producing charcoals that are extremely low in ash is by treatment with H_2F_2 followed by activation. After such preparation, charcoals of the most varied origins were found to be identical with respect to adsorptive capacity.

[159] E. J. MILLER, Colloid Symposium Monographs, Vol. V, New York, 1928; p. 55. References to the original papers are given there.

[160] Compare the comprehensive presentation by A. KELLERMANN and E. LANGE, *Kolloid-Z.* **90**, 89 (1940).

[161] D. TOMASSI, *Bull. soc. chim.* **37**, 197 (1882); M. P. IYER, *J. Indian Chem. Soc.* **8**, 613 (1931).

[162] K. RUEGG, *Kolloid-Z.* **41**, 275 (1927).

with solutions of alkali salts of organic acids, the base is taken up preferentially and the solution becomes acidic.[163] A relevant instance was observed by Zocher.[164] He studied the behavior of lead dioxide (precipitated from lead acetate by chlorine, and then washed free of acid) toward concentrated solutions of alkali chlorides. In contact with such PbO_2, these solutions acquire an alkaline reaction. Obviously, the liberation of the alkali hydroxide results from the preferential adsorption of HCl molecules. This explanation is supported by the fact that nitrate and sulfate solutions do not exhibit a similar behavior. It remains an open question whether the hydrochloric acid taken up initially through an addition adsorption subsequently reacts with the adsorbent. Addition adsorption of hydrolytic products of electrolytes are quite common among solutions of readily hydrolyzable metal salts. Instances include: the retention of lead from lead salt solutions (especially lead acetate) by charcoal or paper; the analogous behavior of solutions of silver salts; the taking-up of iron from ferric solutions by sand.

A proper understanding of polar adsorption, in which the cation and anion of an electrolyte are adsorbed to different extents on a solid adsorbent, requires a clear picture of the orientation of an electrolyte with respect to the surface of a solid. This orientation was mentioned on p. 451 in the discussion of the hydrosol state. In hydrosols, electrically neutral particles become electrically charged through preferential fixation of one ionic species of an electrolyte, while the corresponding counter ion remains in a diffuse outer layer. Therefore, a polarity of the adsorption exists only if the particles, together with their surface, are regarded on the one hand, and the diffuse layer on the other. If, however, the particles along with their double layer are isolated from the bulk of the outer solution, an operation which is quite practical by means of ultrafiltration, the differences in the adsorbability of the ions disappears. Polar adsorption cannot be detected under such circumstances, the adsorption appearing to be apolar. The fixing of an electrolyte on hydrosol particles is often designated as adsorption. However, this is correct only in a limited sense. The retention of charge-determining ions can be regarded as true adsorption, and accordingly the colloid ion is an adsorption system. Of the counter ions, that are distributed in a diffuse layer around the colloid ions, only those can be considered as being adsorptively bound that are situated at distances of approximately molecular dimensions and not much farther from the surface of the solid molecular aggregates. The same orientation of ions of an electrolyte toward a surface, as exists among the freely suspended colloidal particles, must also be assumed

[163] F. E. BARTELL and Y. FU, *J. Phys. Chem.* **35**, 676 (1929).

[164] H. ZOCHER, *Z. anorg. allgem. Chem.* **112**, 64 (1920).

with gels that have been produced from sols by coagulation. In fact, this same assumption must be made regarding all surfaces that are capable of adsorption. If systems that contain adsorbed ions are brought into contact with solutions of electrolytes, there may be an exchange of adsorbed ions (primary as well as counter ions) for ionic species of the solution. This is known as ion exchange or exchange adsorption. It is entirely comparable with the displacement of adsorbed molecules by other more strongly adsorbable molecular species. Whereas a whole molecule is replaced by another in the products of an addition adsorption, only one of the ionic species derived from the molecules of an adsorbed electrolyte is replaced by another kind of ion in exchange adsorption of electrolytes. In the foregoing discussion, stress has been placed on the exchangeability of ions within the bounds of what has been defined as adsorption, *i.e.*, an accumulation of a substance on the surface of a material (an adsorbent) whose interior remains unaltered. Finally, it is logical to regard the following also as a case of exchange adsorption: a solid without previous adsorption of a foreign electrolyte can exchange ions from its surface directly for other ions.

The essence of this type of ion exchange during the adsorption of electrolytes was first recognized by Gans[165] in the action of certain silicates toward salt solutions. These silicates have a marked ability to take up cations of an electrolyte from its solution, and, in exchange, to deliver cations that were contained in the water-insoluble silicate. Such silicates are represented by the natural crystalline zeolites (chiefly aluminum silicates) and also by amorphous silicates, first prepared by Gans, who fused together quartz, kaolin, and alkali carbonate and then thoroughly washed the product. These latter preparations are also called permutits (*permutare* = to exchange) because the ion (base) exchange can be reversed by digesting with a concentrated salt solution that contains the ionic species which was given up by the permutit. Schulze[166] proved that the exchange proceeds smoothly, even at room temperature, and that sometimes, with sodium permutits, the whole of the sodium can be exchanged for other cations. Consequently, when, for instance, a solution of potassium chloride is brought into contact with a sodium permutit, the following schematic reaction can be written:

$$\text{Permutit-O-Na} + \text{KCl} \rightleftharpoons \text{Permutit-O-K} + \text{NaCl}$$
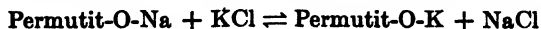
The exchange on a permutit is frequently regarded as an adsorption. However, it should be remembered that an adsorption, by definition, is a

[165] R. GANS, *Jahrb. preuss. geol. Landesanstalt* (*Berlin*) **26**, 175 (1905); **27**, 63 (1906); D.R.P. 174097; *Chem. Centr.* **1906**, II, 728.

[166] G. SCHULZE, *Z. physik. Chem.* **89**, 168 (1915).

purely surface process that leaves the interior of the adsorbent unchanged. Consequently, the complete bulk reaction of a zeolite or permutit is not an adsorption, because no unaltered interior remains after the exchange. If, however, the concept of a surface is extended so that it also includes a thin layer of molecular dimensions without adhering bulk—such a structure patently is presented by permutits—then the complete bulk reaction of a permutit or zeolite could be designated as an adsorption. The writer believes it is better not to consider a bulk reaction of this kind as an adsorption. There can be no doubt, however, that adsorption is intimately involved when an exchange reaction is actually confined to a surface and does not exceed these bounds even after a considerable time. Obviously, the whole gamut of transition instances can lie between the extreme cases that have just been considered. It is expedient to designate the last described exchange as a primary exchange, in contrast to secondary ion exchange in which the ions already held on an adsorbent are exchanged for other ions. Primary and secondary ion exchanges are characterized by a dependence on the particular pH of the solution. This is readily understood since H^+ and OH^- ions manifestly can compete with other ionic species.[167]

The various kinds of exchange adsorption have a common characteristic: when an ion disappears from the solution, another appears in its place. If the latter is H^+ or OH^- ion, the case is one of hydrolytic adsorption. In such instances of change of pH, it cannot be declared categorically that the H^+ or OH^- ions have issued from the solid adsorbent in exchange for other ions. As was shown earlier, hydrolytic adsorption, in the restricted sense, may arise from apolar adsorption of an hydrolysis product. Under such circumstances, the H^+ or OH^- ions that enter the solution do not come from the adsorbent but rather from the water molecules of the solution. The following example may illustrate the possibilities that should be kept in mind when electrolyte adsorptions are involved. If the hydrated manganese dioxide produced by the action of manganous sulfate with permanganate or persulfate in weakly acid solution is washed free of acid, and then added to a neutral solution of potassium chloride, the solution becomes acid. This acidic reaction may arise in three different ways, which correspond to the previously cited possiblities of electrolyte adsorption: (a) Hydrolytic or fission adsorption of potassium chloride may occur, in that the KOH resulting from hydrolysis of the salt may be adsorbed on the MnO_2, possibly with subsequent formation of potassium manganite. (b) Ion exchange may take place in that K^+ ions replace H^+ ions that were firmly held in the acidic $MnO(OH)_2$. (c) An ionic exchange of the follow-

[167] Compare S. M. HAUGE and J. J. WILLAMAN, *Ind. Eng. Chem.* **19**, 943 (1927).

ing kind may be involved: manganese dioxide may irreversibly adsorb sulfuric acid with SO_4^{--} ions as the inner layer and the accompanying cations, that normally function as counter ions, are exchanged for K^+ ions.

It is a rather common practice to speak simply of the activity of a solid adsorbent without taking into consideration which portions of the free surface participate in the adsorption process. The example, just cited, of adsorption on manganese dioxide demonstrates, however, that, in the adsorption of electrolytes especially, it is necessary to differentiate between the activity of a pure adsorbent due to addition or exchange adsorption and the activity of electrolytes that are already held on an absorbent. Such electrolytes can exchange their ions for those of newly arriving electrolytes. When solids are formed by precipitation, the product frequently results from the coagulation of colloidal dispersions that represent intermediate stages between solution and precipitate. In such cases, it must be remembered that. both the colloidally dispersed particles and the product obtained from them by coagulation are adsorption systems. In fact, if considered by itself, the coagulation *per se* is a process of ion exchange, at least in part. The varieties in action of an electrolyte that is being adsorbed on the particles of a precipitate, either during or after the formation of the latter, cannot be strictly differentiated from each other except by very discriminating studies. This is particularly true with respect to establishing whether exchanged ions originate in the surface of the solid adsorbent or whether they come from ions that were previously adsorbed there. Natural or technical products that function as adsorbents often carry water-insoluble·contaminants or admixed materials that are tenaciously held by either chemical or mechanical forces. Such extraneous materials frequently are responsible for most or even all of the adsorptive powers of the system. Under such circumstances, the material which is called the adsorbent actually is nothing but a framework, possessing little or no activity of its own. Such possibilities must be considered when dealing with carbons, papers, minerals, glass, *etc.*[168] The method of preparation or origin of such adsorbents is often reflected in characteristic fashion in the degree to which they adsorb certain materials. For instance, carbons can be distinguished by the extent of their action toward methylene blue. Sometimes, even slight differences in the physical structure, or the presence of impurities in amounts below the limits of ordinary analytical detection, can be of great significance with respect to the adsorption capability of solids. Filter papers that serve for quantitative purposes have been specially purified; they consist essentially of very high grade

[168] I. M. KOLTHOFF, *Pharm. Weekblad* **57**, 1571 (1920); *Kolloid-Z.* **30**, 35 (1922).

cellulose. Hence, it might be presumed that they would have approximately identical adsorptive properties. However, Effront's[169] findings with 7 varieties of such papers showed that their adsorption of pepsin ranged from zero to 100%. The behavior of the proteins that accompany pepsin as contaminants is noteworthy. Filter paper which adsorbs no pepsin retains proteins quantitatively, whereas paper which adsorbs pepsin quantitatively leaves proteins undisturbed in solution. The reasons for the diverse adsorbability of pepsin on filter paper are not known as yet, since no differences have been established for the varieties of papers employed in these studies either with respect to their ash contents or in their analytically detectable impurities.[170]

Although natural and technical products, when dispersed highly enough, often can be characterized by a definite extent of their adsorption ability, this is not true of adsorbents that are undergoing a more or less rapid aging process. This class of adsorbents includes practically all solids produced by precipitation, and especially those with gel-like structures. The adsorption capability of such products often decreases to a very marked extent during the aging. A pertinent instance is the taking up of As_2O_3 by hydrous ferric oxide. This process, which was first observed by Bunsen in 1834, was long considered to be due to the formation of basic ferric arsenite in the sense of the production of an independent phase. Actually, as Biltz[171] showed, it is a reversible adsorption of As_2O_3.[172] The adsorption capacity of the hydrous ferric

[169] J. Effront, *Ann. bull. soc. roy. sci. med. nat. Bruxelles* **4**, 24 (1926).

[170] In this connection, reference should be made to the observations of S. Tabak [*Quimica (Brasil)* **1**, 146 (1946)]. He found that if a drop of water is allowed to spread on quantitative filter paper and the latter is then heated to 150–170°C., a brown ring develops at the boundary of the fleck. This ring is probably due to traces of water-soluble contaminants that move with the water through the capillaries of the paper and, even at the temperature of the experiment, catalytically hasten an incipient decomposition (charring?) of the cellulose. F. Feigl and H. W. Zocher (unpublished studies) observed that quantitative filter papers, depending on their origin, contain varying amounts of a blue-fluorescing, water- and alcohol-soluble material. The latter also accumulates in the peripheral zone when a drop of water or alcohol spreads on the paper. The fluorescence of paper and the fluorescence of the boundary zone produced by the capillary spreading of water or alcohol are intensified by warming. The fluorescing compound that accumulates at the edge of a fleck exerts no influence on the decomposition which sets in at low temperatures. These observations, which prove that quantitative filter paper by no means consists of pure cellulose, may possibly be connected with the effects observed by Effront (*loc. cit.*).

[171] W. Biltz, *Ber.* **37**, 31, 38 (1904).

[172] It would be in accord with the viewpoint adopted here if the reversible adsorption of As_2O_3 were also a formation of arsenite; however, with the essential criterion that no new phase is produced. Rather, the combination of the iron atom and the arsenite radical remains in the phase association of the hydrous ferric oxide.

oxide is not constant; it falls as the aging progresses, and the dried material is almost inactive.[173] Biltz coined the very apt term "condition affinity" for the varied adsorptive behavior of the hydrated iron oxide. In the light of the present knowledge of adsorption, condition affinity is nothing but the reflection of the variation in the number of surface atoms and molecules of solids that can participate in the process of an addition- or exchange adsorption. Since their number decreases when the adsorbent ages, it is easy to see that adsorption reversal, *i.e.*, the liberation of adsorbed materials from aging precipitates, corresponds to this decrease in the condition affinity.

The preceding discussion has as its object the characterization and elucidation of adsorption processes. It is evident that adsorption, one of the fundamental processes of colloid chemistry, cannot be an irrelevant factor in analytical operations. The contamination of precipitates through adsorption of dissolved materials both during and after the precipitation process and the decrease in concentration of dissolved materials as a result of adsorption, which, in extreme cases, can eventuate in their total removal or disappearance from the solution, are effects which are closely related to the specificity, selectivity, and sensitivity of tests, or that can be brought into a very close relationship to these characteristics. The adsorption effects that are the most significant from the standpoint of analytical procedures can be either undesirable or desirable. On one hand adsorption may be a deleterious side effect, whose occurrence should be suppressed as much as possible or whose ultimate elimination is a prime objective. On the other hand, adsorption may be the desired main effect which can be utilized directly or indirectly. Adsorption is a handicap in all analytical procedures whose object is to secure the deposition of pure materials by precipitation reactions. Considerable errors can occur in such cases when marked adsorption occurs. There is a limit to the removal of strongly adsorbed materials by washing with pure water, since every solid exhibits some solubility and, in addition, peptization is always a possibility. Frequently, this difficulty is obviated by washing precipitates with solutions of ammonium salts or acids. Such added materials may act in two ways. They may be used solely to prevent a peptization and thus make possible a thorough washing (desorption) with large amounts of water. However, they may also serve to displace an adsorbed ionic species, either because their own ions are more strongly adsorbed or, in case the adsorbabilities are approximately equal, by virtue of the higher ionic concentration in the wash liquid. A model example is provided by the following observation made

[173] Compare K. C. Sen, *J. Phys. Chem.* **31**, 419 (1927).

by Charriou,[174] in which the occurrence of an ion exchange can actually be seen. When ammonium hydroxide is added to aluminum salt solutions that also contain chromate, the precipitate is distinctly yellow because of the adsorption of CrO_4^{--} ions. The latter are not removed, or only incompletely, by washing with hot water or solutions of ammonium halides, nitrate, or acetate. In contrast, ions, such as CO_3^{--}, SO_4^{--}, $C_2O_4^{--}$, PO_4^{---}, AsO_4^{---}, which are more strongly adsorbed by the precipitate, immediately and completely displace the CrO_4^{--} ions, and the yellow color disappears. The expulsion of chromate by washing with 5% ammonium carbonate solution is of practical importance, since the precipitation in chromate-bearing aluminum solutions by means of ammonium carbonate leads directly to chromate-free alumina. It should also be noted that ion exchange not only serves to purify precipitates, but also may make available for qualitative tests and quantitative determinations materials that are set free from the adsorbent. For instance, van den Hoeven[175] showed that accurate quantitative determinations of sulfate in leather are made possible by washing the sample with 8% NaH_2PO_4 solution, which displaces any sulfuric acid (or SO_4^{--} ions) irreversibly adsorbed on the leather.

The visible separation of precipitates is always preceded by a sol stage in which the colloidally dispersed particles possess an enormous specific surface, which is partly retained if the subsequent precipitates are gelatinous. Consequently, deposition of perfectly pure products can never be expected. In the most favorable case, adsorption of water occurs during the precipitation process, but frequently this is accompanied by the adsorption of cosolutes, as well as of molecules or ions of the precipitant. Hence, according to the kind and extent of the adsorption, there can be serious impairment not only of the purity of a precipitate, a matter of grave importance in gravimetric determinations, but also of the specificity or selectivity of a precipitation reaction. Such detrimental effects can often be lessened by employing appropriate expedients, as has been pointed out previously. Furthermore, the constantly growing number of new analytically useful precipitation reactions makes it possible, in almost every case, to choose those in which there is little or no likelihood of serious injurious adsorption.

Empirical studies are indispensable when the adsorptive impairment of a precipitation reaction is to be measured. This is necessary because reliable predictions are hardly possible in view of the selective character of adsorption and its dependence on the conditions obtaining during the

[174] A. Charriou, Compt. rend. 176, 679, 1890 (1926).
[175] C. van den Hoeven, Chem. Weekblad 19, 556 (1922).

precipitation (pH, nature and concentration of cosolutes, *etc.*).   In general, the use of organic precipitants that lead to the production of inner complex salts involves less danger of adsorption than the employment of reactions that result in insoluble electrolytes.   This is an additional reason for the desirability of constantly continuing the search for new organic precipitants which, as a class, are known to exhibit notable selective salt-forming abilities.   Perhaps the exceptional behavior of inner complex compounds is connected with the fact that certain types of these compounds have practically no electrolytic character.   This is reflected in the surprisingly wide-spread solubility of inner complex compounds in organic liquids.   Experience has shown that adsorption influences are far more to be feared among difficultly soluble compounds with pronounced electrolytic character.   Certain regularities that play a role here are expressed by the Paneth-Fajans-Hahn rule.   This states: "An ion is strongly adsorbed by an insoluble electrolyte if the ion forms an insoluble or slightly dissociated compound with the oppositely charged ions of the lattice of the electrolyte."   Accordingly, every precipitate adsorbs the respective precipitating ion.   The adsorption is enhanced if there is also present a strongly adsorbable, oppositely charged ion derived from a third electrolyte.   According to Fajans, hydration, ionic radius, and deformability of the ion to be adsorbed, also exert an influence.   The adsorption increases with decreasing hydration and with diminishing ionic radius, whereas rising deformability promotes adsorption.   The Paneth-Fajans-Hahn rule assumes a direct adsorption of ions on a lattice by virtue of the activity of auxiliary valences of the ions situated on the surface of the lattice.   Accordingly, this is a process through which the electrical condition of the surface must be altered.   In contrast, Kolthoff[176] stresses the exchangeability of a lattice ion of the surface of a slightly soluble electrolyte by another ion, the surface charge remaining unchanged.   Thus, he gives the following expression for the adsorptive uptake of lead ions by barium sulfate (see p. 641):

$$\frac{\text{Pb (surface)}}{\text{Ba (surface)}} = K \frac{\text{Pb (solution)}}{\text{Ba (solution)}}$$

In this, K is the distribution coefficient of the lead between the solution and the surface.   Direct ionic adsorption and exchange of ions doubtless are fundamental events in the total process of any adsorption, and must be taken into account in analytical procedures.   Consideration must also be given to the adsorption of undissociated molecules, the preference for certain portions of the surface as adsorption sites, the modification of the reactivity of adsorbed materials (see p. 521), and reactions in the adsorb-

[176] I. M. KOLTHOFF, *J. Phys. Chem.* **40**, 1027 (1936).

ate.   Finally, it may not be forgotten that a precipitate, functioning as an adsorbent, does not itself remain unchanged, but is being subjected to alterations (see Chapter XI).   All these considerations indicate the complexity of "analytical adsorption," which is also reflected in a selectivity of adsorption processes that is often truly amazing.   The heights that can be reached in such selective adsorptions are illustrated by the two following examples that involve inorganic compounds which are quite similar to each other.   If a stannic solution, which also contains PO_4^{---} ions, is treated with hydrogen sulfide, the stannic sulfide precipitate always contains considerable amounts of phosphorus.   Hence, it is not possible to secure satisfactory results for phosphate by analyzing the filtrate from a SnS_2 precipitation.   However, Kikuchi[177] found that phosphate can be quantitatively determined in tin salt solutions provided the tin is reduced (e.g., by metallic zinc) previous to the sulfide precipitation.   Another example, that illustrates the selectivity of adsorption very definitely, is taken from Hahn's[178] study of the behavior of purpurin toward the alkali earth oxalates.   Only calcium oxalate is tinted by this hydroxyanthraquinone dye, whereas barium and strontium oxalates are unaffected.

The impairments of precipitation reactions by adsorption[179] are largely offset by the benefits which may accrue from the utilization of adsorption phenomena.   For the most part, such advantages reside in the fact that materials in true or colloidal solution are adsorbable on suitable adsorbents and, in fact, are frequently taken up from even very dilute solutions.   This removal sometimes makes it possible to accomplish a

[177] S. KIKUCHI, J. Chem. Soc. Japan 43, 329 (1922).

[178] F. L. HAHN, Ber. 65, 207 (1932).

[179] Adsorption can interfere not only in precipitation reactions but also in filtrations occurring in the course of analytical separations.   It is well known that the first portions of a filtrate that has passed through paper frequently may not be used for quantitative analyses, since adsorption by the paper can result in decreases in concentration.   Irreversible adsorption is plainly discernible when solutions of basic dyes (e.g., methylene blue) are passed through filter paper.   Accordingly, the filtration of colored solutions through paper for purposes of subsequent colorimetric determinations may introduce serious errors.   An instance is the filtration of red $Fe(\alpha,\alpha'\text{-dip})_3$ salt solutions during which the pH must be kept at a predetermined value in order that the adsorption of the red complex ion will be held to a tolerable minimum [compare E. ASMUS, Z. anal. Chem. 122, 81 (1941)].   A. SCHLEICHER [ibid. 121, 90 (1940)] found that, in the usual barium sulfate method of determining sulfate, the filtration of the suspension, that naturally contains an excess of barium chloride, leads to the adsorption of barium by the filter paper.   When the latter is ashed, the adsorbed material is weighed along with the rest of the ignition residue and, hence, high results are obtained.   However, if the paper is washed beforehand with moderately strong hydrochloric acid, so that the adsorption areas of the paper are occupied by tenaciously held H^+ ions, and then rinsed with hot water, the interference becomes inconsiderable.

difficult separation which can be used for qualitative as well as quantitative purposes. At times, an adsorbed material can be identified right on the adsorbent or, with greater certainty, after separating it from the adsorbent, or after destroying the adsorbent. These latter two methods are required if a quantitative determination of the adsorbed material is to follow. The isolation of materials through the aid of adsorption can be carried out in two ways: (a) direct addition of the adsorbent to the solution; (b) production of the adsorbent in the adsorption medium. Both of these types of adsorption have prototypes in technical chemistry. Familiar examples are the widely used decolorizing action of charcoal, and the use in water-purification of alumina produced by the addition of aluminum sulfate and lime to the water.

Skey[180] seems to have been the first to realize the analytical importance of the removal of small amounts of dissolved materials by means of adsorption agents. He stated that antimony and arsenic are so completely removed by charcoal from moderately strong hydrochloric acid that the sensitive Reinsch test for these elements fails. He went so far as to recommend that his findings be applied in the purification of commercial sulfuric and hydrochloric acids. Because of their marked ability to adsorb materials of the most diverse natures and from a wide variety of solvents, finely divided, purified carbons have been used for many years not only in studies of adsorption,[181] but also as adsorbents in analytical procedures. For example, Cole[182] adsorbed lactose on blood charcoal, which was then treated with warm acetic acid (adsorption displacement) and the osazone test carried out on the extract. Other adsorbents have been used for analytical purposes. For instance, Vanino[183] found that barium sulfate decolorizes metal hydrosols, but leaves certain dye solutions unchanged. He recommended this diverse behavior for analytical tests. However, later studies[184] showed that colloidally dispersed dyes are also adsorbed by barium sulfate. The quantitative removal of tannins by shaking their aqueous solutions with hide powder is the basis of a widely used method of determining tannins.[185]

The analytical utilization of the adsorption on solids of materials from true and colloidal solution may involve the types of adsorption that were discussed in the foregoing paragraphs, i.e., addition adsorption of

[180] W. SKEY, Chem. News 17, 157 (1868); 36, 6 (1877).

[181] Concerning activated carbons compare H. HERBST, Kolloid-Beihefte 42, 184 (1935); H. FISCHER, ibid. 42, 125 (1935).

[182] S. W. COLE, Biochem. J. 8, 134 (1914).

[183] L. VANINO, Ber. 35, 662 (1902).

[184] G. ROSSI and G. SCANDELLARI, Gazz. chim. ital. 63, 261 (1933).

[185] A. W. THOMAS and M. W. KELLY, Ind. Eng. Chem. 15, 1148 (1923).

molecules and molecular aggregates, and exchange adsorption of ions. Ion exchange predominates in the adsorption of electrolytes from aqueous solution. As has been pointed out, there are two kinds of ion exchange: (a) the exchange of ions that are already adsorbed on an adsorbent; (b) the exchange of ions that are present in the solid lattice of an insoluble salt. In the latter case, it is common practice to speak of the permutit function of an adsorbent. If neutral or weakly acid solutions of ammonium salts are shaken with natural or artificial sodium permutits, the NH_4^+ ions replace Na^+ ions. If the solution that is thus rendered free of ammonium salts is decanted from the resulting ammonium permutit, and the latter then placed in alkaline Nessler solution, the NH_4^+ ions are displaced by K^+ ions. The liberated ammonia then forms the familiar yellow-brown $Hg_2NH_2I_3$ which can be estimated colorimetrically. Alternatively, the ammonium permutit can be kjeldahlized. The latter method is imperative if, for example, the ammonium adsorption is from a colored vegetable extract, because basic coloring matters will also be adsorbed and they, likewise, will be driven out of the adsorbent by the alkaline Nessler reagent. Consequently, the Folin-Bell[186] procedure is particularly interesting because it makes possible a separation of ammonium salts from other nitrogenous compounds, such as aniline, phenylhydrazine, urea, *etc.*, which are converted into ammonium salts if the Kjeldahl procedure is applied directly. However, this selectivity does not extend to such lengths that, for instance, ammonium salts can be separated from salts of methylamine. Nonetheless, a distinct decrease in the ability to replace the sodium in permutit has been established in the series: mono-, di-, and trimethylamine.

A very interesting adsorption reaction, which may be considered as an ion exchange, was reported by Lloyd[187] in his study of the behavior of hydrated aluminum silicate (prepared from fuller's earth) toward acid solutions of alkaloids. The latter are taken up completely, and the adsorbate, after washing with water and alkalization, will give up the alkaloid to a suitable solvent. Obviously, this procedure which can be used in actual analytical practice, rests on the fact that the ammonium-like alkaloid cations contained in the acid solutions replace the hydrogen ions in the solid acid silicate and, in turn, are displaced by the base with production of the alkali salt of the silicate and the free alkaloid. If it is recalled that water solutions of polyatomic acids and complex acids (*e.g.*, phosphomolybdic and phosphotungstic acids) are invariably

[186] O. Folin and R. D. Bell, *J. Biol. Chem.* **29**, 329 (1917); compare also G. Klein and K. Tauböck, *Biochem. Z.* **241**, 413 (1931).

[187] J. U. Lloyd, U. S. Patent 1,048,712 (1912); *J. Am. Pharm. Assoc.* **5**, 318 (1916); see also S. Waldbott, *J. Am. Chem. Soc.* **35**, 827 (1913).

alkaloid precipitants, the action of Lloyd's reagent is quite understandable. It involves the formation of alkaloid salts with the acid complex silicate, but, in this case, the action occurs on the surface of the adsorbent and is confined to this portion of the reagent.[188] Accordingly, the chemical character of adsorption is exhibited particularly well in this instance. It is rather remarkable that the adsorption of alkaloids on Lloyd's reagent occurs even in the presence of sugars and salts, and hence is quite specific. Bergdoll and Doty[189] have found that basic amino acids, such as lysine and histidine, are taken up from hydrochloric acid solution by Lloyd's reagent, whereas non-basic amino acids are not adsorbed. They have used this finding in developing a valuable method for separating basic amino acids from mixtures by means of chromatographic analysis. It is quite probable that this procedure involves an exchange adsorption of the same type as that which operates in the adsorption of alkaloids on Lloyd's reagent.

Synthetic resins can participate in ion exchange adsorptions. Adams and Holmes[190] reasoned that, since the phenolic OH-group is not involved when insoluble resins of the Bakelite type are formed, the H atom of the OH-group should be free to ionize in the usual way and therefore be available for ion exchange. Actual trials demonstrated that such phenol-formaldehyde resins do possess base exchange activity and permit ion exchange when treated with solutions of inorganic salts. Amine-formaldehyde resins likewise adsorb acid molecules from aqueous solutions. Therefore, synthetic resins can be regarded as insoluble macromolecular electrolytes which, despite their low solubility, are capable of metathetical reactions with ordinary electrolytes. This discovery has opened a new field of chemical applications of synthetic resins as well as presenting a new method of differentiating resins on the basis of their ion exchange properties.[191] Cranstone and Thompson[192] have applied the exchange adsorption between cupric ions and synthetic resins in their method of determining traces of copper in milk.

The procedure in which solid adsorbents are added to solutions and

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[188] In accordance with this view it was shown that $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot aq$, which is not soluble in water or acids, exchanges ammonium for alkaloid cations when it is shaken with solutions of alkaloid hydrochlorides. Perhaps this offers the possibility of trace-gathering of alkaloids (unpublished studies by F. FEIGL and I. D. RAACKE on caffein, theobromine, strychnine, and quinine).

[189] M. S. BERGDOLL and B. M. DOTY, *Ind. Eng. Chem., Anal. Ed.* **18**, 600 (1946).

[190] B. A. ADAMS and E. L. HOLMES, *J. Soc. Chem. Ind. (London)* **54**, 1 (1935).

[191] Compare R. J. MYERS, "Synthetic Resins Ion-exchange" in Advances in Colloid Science, Vol. 1, p. 317. New York, 1942.

[192] H. A. CRANSTONE and J. B. THOMPSON, *Ind. Eng. Chem., Anal. Ed.* **18**, 323 (1946).

then filtered off is now being largely replaced by the technique in which the solution is allowed to percolate through a tube charged with a suitable adsorbent. The adsorbable materials are retained as distinct zones in the adsorption column, and it is thus possible to separate even a number of materials from each other by the action of the same adsorbent. This process of chromatographic analysis has become exceedingly important for the separation of organic compounds. It will be discussed in considerable detail in the last section of this chapter.

As has been stated, an alternative procedure is to produce an adsorbent for the materials to be removed by carrying out a precipitation reaction in the adsorption medium itself. It is clear that this method will amply meet the requirement of providing an adsorbent with a well developed surface and a very high state of division. Consequently, the procedure of capture by a precipitate in *statu nascendi* often makes possible the quantitative fixation of small or even exceedingly tiny quantities of dissolved materials. This effect is known as collector action of precipitates or trace gathering. The particular precipitation reaction that results in the formation of the adsorbent thus, to an extent, induces a second precipitation that would not occur *per se* as an isolated phenomenon, or that would not take place because the concentration is too low. Pertinent instances were cited in Chapter V, and further reference to this action will be given in Chapter XI. The collector action of fresh precipitates is of great importance in the detection and determination of microquantities of materials. In the absence of this effect, trace analysis by the wet method would either be impossible or would necessitate the use of procedures that are both tedious and subject to grave sources of error. The collector action of precipitates may involve the adsorption of ions or molecules of the material that is present in traces, as well as the adsorption of colloidally dispersed particles. However, additional effects, such as the formation of mixed crystals and complex salts, are also possible.

Because of the great analytical importance of the phenomenon, the foregoing discussion has dealt solely with adsorption from true or colloidal solution on the surface of solids. However, in this connection it must not be forgotten that adsorption as a general surface phenomenon, or better as an interfacial phenomenon, is not limited to the surface of solids. An air-liquid or liquid-liquid interface can also be the site of an adsorption. The solutions which are encountered in analytical procedures possess such small free liquid surfaces that in practice they may be neglected with respect to any accumulation of materials because of adsorption. The conditions are different, however, when through the formation of a foam a significant extension of surface is brought about.

Then there can be a very marked concentration of dissolved material in the foam. This was first shown by Benson[192a] with an amyl alcohol-water mixture, which was made to foam by passing air through it. The foam was collected in a separate vessel, and, after breaking, it produced an amyl alcohol-water mixture, whose alcohol content was about 6% higher than at the start. Deutsch[192b] discovered the strikingly simple experiments which demonstrate, in a most impressive manner, the adsorption of dissolved materials at the boundary between water and air, or between water and an immiscible organic liquid. Vigorous shaking of 0.01 N hydrochloric acid solution containing thymol blue produces a red color in the froth, which is much deeper than that of the original solution. In other words, the red (undissociated) form of the indicator is enriched in the foam. If the water solution is shaken with benzene or ligroin instead of air—thus forming a water-benzene (ligroin) boundary—a beautiful red emulsion results, whose color is much deeper than that of the original aqueous solution. When the froth or emulsion breaks, the liquids separate and the water solution is reformed with its original color.

Solutions of other indicators, basic or acid, lend themselves to similar experiments, which can also be carried out in alkaline pH ranges. The tone and depth of an aqueous solution of an indicator are determined by the pH-dependent equilibrium, which exists in the solution between the various molecular and ionic species of the indicator. Accordingly, if a deepening of color occurs when a froth or an emulsion is formed, an increase of the particular colored constituent is indicated. Hence, the experiments of Deutsch show that there is not only an accumulation of dissolved material at a liquid interface; they also demonstrate that one constituent can be preferentially adsorbed from a dissociation equilibrium. Naturally, this is only possible through disturbance of the equilibrium, which is then restored in the aqueous solution. Therefore, it may be said that the dissociation equilibrium in the boundary differs from that in the body of the solution, and that this equilibrium represents a lower dissociation constant for the indicator than that which applies when the indicator is in aqueous solution. Selective adsorption is frequently exhibited by solid adsorbents; for instance, in hydrolytic adsorption in which a certain component is preferentially adsorbed from an hydrolysis equilibrium. The examples just cited of an adsorption at liquid-liquid or liquid-air boundaries, which probably should be regarded as addition adsorptions, therefore illustrate, with respect to an accumulation of materials, a fundamental similarity to the adsorption on the

192a C. BENSON, *J. Phys. Chem.* **7**, 532 (1903).
192b E. DEUTSCH, *Ber.* **60**, 1036 (1927); *Z. physik. Chem.* **136**, 353 (1928).

surfaces of solids. The adsorption on liquid surfaces was employed by Wo. Ostwald in the so-called foaming analysis to accumulate dissolved materials. This will be referred to again in the last section of this chapter, i.e., in the discussion of the methods of adsorption analysis.

The adsorptive behavior of solid surfaces toward gases deserves at least a brief mention here. It is the same as that toward dissolved materials, i.e., the surface may be the vestibule for the penetration of gases into the interior (absorption) or there may be local accumulation to greater degrees on the surface than in the gas space (adsorption). Likewise, when gases are adsorbed it is necessary to differentiate between an addition adsorption and an adsorption through the formation of reaction products between gas and solid on the surface of the solid without development of a new phase. The addition adsorption of gases corresponds in principle to the production of molecular compounds through the action of residual valences, or even a binding through van der Waal forces, somewhat as in the condensation of vapors, for example. In addition to real adsorption, which occurs also on smooth surfaces, it is necessary also to take into consideration a condensation of gases accompanied by the filling up of the cavities when dealing with materials that possess capillary hollow spaces of 2μ or less (activated charcoals, silica gel, etc.). This is the so-called capillary condensation which, from a quantity standpoint, accomplishes more than the adsorption. If the cavities approach molecular dimensions, it becomes difficult to differentiate between adsorption and capillary condensation. Adsorption, absorption, and capillary condensation, as well as their reversals (desorption) play an important part in gas analysis. The province of specificity, selectivity, and sensitivity, which is the center of interest of this book, involves the adsorption of gases only in the relatively infrequent cases of the use of gaseous reagents. In such instances, the significance does not reside in the accumulation of a gaseous reagent through adsorption, but rather in any possible enhancement of reactivity (activation) secured through adsorption. This point will be discussed in the next section.

Modification of the Reactivity of Materials by Adsorption

The discussion in the preceding section of the various mechanisms of adsorption processes particularly stressed the accumulation of material on free surfaces. Constant reference was made there to the analytical significance of adsorption and, with the aid of numerous examples, it was shown that this phenomenon leads to contamination of precipitates and to the disappearance, to a greater or lesser extent, of dissolved materials when their solutions are in contact with suitable adsorbents. The closing section of this chapter will deal, in considerable detail, with the

methods of adsorption analysis and with those spot tests in which the
selective accumulation of materials through adsorption is extensively used
in the separation of constituents of a solution.   However, several other
interesting effects that are connected with adsorption should be discussed
beforehand in three separate sections, in addition to certain statements
given previously in this chapter.   These effects are: (1) modification
(lowering or raising) of the reactivity of an adsorbed material or the
adsorbent in an adsorbate; (2) color changes that result from adsorption;
and (3) formation of so-called adsorption compounds.   Many findings
along these lines were made in purely colloidal studies that had no
analytical objectives.   As in other sections of this chapter, colloid chemi-
cal investigations are also cited here inasfar as they provide an insight
into effects that are properly a part of the discussion concerning the
specificity, selectivity, and sensitivity of reactions.

Reitstötter[193] made the interesting observation that the gel obtained
by flocculating an Al_2O_3 sol by means of potassium ferrocyanide does not
produce Prussian blue at once upon the addition of dilute ferric chloride
solution; there is a distinct lag in the appearance of the color.   In other
words, the normal immediate ionic reaction is not shown by the adsorbed
$Fe(CN)_6^{----}$ ions; instead, they react sluggishly.   It was further shown
that Prussian blue is produced immediately if the Al_2O_3 sol is treated,
either before or after adding the ferrocyanide, with salts whose anions
are more strongly adsorbed than $Fe(CN)_6^{----}$ ions.   The adsorption of
the latter is thus impaired or they are displaced from the surface of the
Al_2O_3, and in this wise the conditions for the reaction of freely moving
ions are reestablished.   It was pointed out on p. 501 that Congo blue
sol adsorbed on Al_2O_3 gel slowly goes over into the red aluminum salt of
Congo acid.   Weiser and Radcliff[194] found that the adsorbed Congo
blue sol is transformed, by dilute alkali, into the red sodium salt much
more slowly than when the Al_2O_3 is not present.   The retarding influence
of an adsorption on the rate of a reaction is unmistakable here.   With
respect to the phenomenon of a modification of the reactivity of materials
when adsorbed, it makes no difference, in principle, whether the adsorbent
is in the form of a gel or a sol, in which latter condition it ordinarily pre-
sents a still greater surface area.   Consequently, the statements and
examples of colloid masking given on p. 474 should be consulted in this
connection.   The cases cited there invariably presented a diminution in
the reactivity of the adsorbed materials.

It is natural to assume that the union between the adsorbed material

[193] J. REITSTÖTTER, *Kolloid-Z.* **21**, 197 (1917); H. FREUNDLICH and J. REITSTÖTTER,
ibid. **23**, 23 (1918).
[194] H. B. WEISER and R. S. RADCLIFF, *J. Phys. Chem.* **32**, 1875 (1938).

and the adsorbent in an adsorbate is responsible for the alteration of reactivity. However, the mere fact that these materials are linked together is not the sole factor; the particular type of linkage is obviously a vital factor. This is shown by Miller's[195] studies of the adsorption of acids on carbon. He found that, when the quantities of acid and carbon are in such proportion that irreversible adsorption of acid ensues,[196] the acid loses its ability to invert sucrose. Since this inversion is an action of H^+ ions (and is proportional to the H^+ ion concentration) he concluded that when acids are adsorbed on carbon, entire molecules of the acids, rather than their ions, are taken up from the aqueous solution. Accordingly, the corresponding ionic reactions will not occur or will be retarded when molecular adsorption of acids has taken place. If the adsorption of hydrochloric acid is considered from this standpoint, it is logical to expect that molecular adsorption from the dilute acid solution will result in a strengthening of those types of reaction which are peculiar to the HCl molecules. An instance is the action of hydrochloric acid on manganese dioxide: $MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_2 + Cl_2$. This reaction proceeds with considerable velocity only when concentrated hydrochloric acid is employed, a fact that points to the necessity of having HCl molecules available for the redox reaction. Lang[197] found that the presence of even small amounts of silver chloride [other silver halides act similarly] suffices to cause even dilute hydrochloric acid to enter into redox reaction with Mn^{IV}, Mn^{III}, Ce^{IV}, and chromic acid. The probable reason for this activation of the hydrochloric acid is that the silver halides adsorb hydrochloric acid in its molecular form, and the acid in the adsorbate reacts toward the foregoing materials as though it were dissolved molecularly. This example is taken from the great field of heterogeneous catalysis, where the enhanced reactivity of adsorbed materials must always be taken into consideration. Chapter V contains still other examples of specific and selective tests which are based on the analytical use of heterogeneous catalysis, in which, therefore, advantage is taken of the enhanced activity of adsorbed materials.

The foregoing discussion has dealt with the change in reactivity undergone by materials when they have been adsorbed. However, cases are known in which the adsorbent component of an adsorbate exhibits an altered reactivity. In most of such instances the reactivity is lessened, a result that is understandable in view of the fact that the adsorption layer shields the underlying portions of the adsorbent from

[195] E. J. MILLER and S. L. BANDEMER, *J. Am. Chem. Soc.* **49**, 1686 (1927).

[196] This is the case with 2 g. blood charcoal plus 5 ml. $N/50$ HCl, H_2SO_4, HNO_3, or 10 ml. $N/50$ acetic, oxalic, benzoic, or salicylic acids, *etc.*

[197] R. LANG, *Ber.* **60**, 1389 (1927).

chemical actions. The possibility should not be excluded that the divergent behavior toward acids of materials which are precipitated together, e.g., sulfides (see Chapter V), may be partly due to such effects. Observations by Mann and his associates[198] are interesting in this connection. They found that small quantities of aliphatic and aromatic amines retard, through adsorption, the corrosion of iron (steel) by 1 N sulfuric acid. The efficacy decreases from tertiary to primary amines. The protective action is very considerable; it may cut down corrosion as much as 99.9%. A relevant phenomenon that is both interesting and capable of analytical employment is discussed in Chapter XI, under the heading "Protective Layer Effects." In such cases, a precipitate which is finely dispersed in paper is shielded against attack by a coating consisting of small amounts of more resistant materials. The formation of adsorption layers may play a role here also. The passivity of metals, which is especially displayed in resistance toward attack by acids, belongs in this category. Such passivity is due to the formation of a protective surface film of oxide that is absorptively fixed on the metal. Technical use is made of such coatings. For instance, iron is made passive (parkerized) and aluminum is anodically oxidized, as a preliminary step to fixing dyes. Various chemical industries employ equipment lined with lead, which has been covered with a protective film of lead sulfate.

Although only a few instances have been found as yet, cases are known in which the reactivity of an adsorbent in an adsorbate is heightened. Almost a century ago, Vogel[199] called attention to the fact that silver bromide prepared by the action of excess silver salts on bromides is far more light-sensitive than silver bromide produced by the action of excess bromides on silver salts. It is now known that the former preparation contains adsorbed Ag^+ ions, while the latter carries adsorbed Br^- ions. Furthermore, silver halides are made more light-sensitive by the presence of adsorbed elementary silver and silver sulfide. The sensitizing of silver halides through the adsorption of certain acid and basic dyes is extremely important to photography. Light-stability is an important factor with respect to the evaluation of lithopones (i.e., $BaSO_4 + ZnS$).[200] Weiser and Garrison[201] found that ZnS is made light-

[198] C. A. MANN, B. E. LAUER and C. T. HULTIN, Ind. Eng. Chem. **28**, 159, 1048 (1936).

[199] H. A. VOGEL, Ann. Phys. **119**, 497 (1863).

[200] Zinc lithopone is prepared by the wet method through the reaction: BaS + ZnSO_4 → BaSO_4 + ZnS. It exhibits marked deviations from the properties of a mere mixture. Colloid chemical factors play a role in the preparation. Compare C. A. MANN, Colloid Symposium Monograph, Vol. III, p. 247. New York, 1925.

[201] H. B. WEISER and A. D. GARRISON, J. Phys. Chem. **31**, 1238 (1927).

sensitive (darkens) by adsorbed Zn^{++} ions and that a certain crystalline structure is essential to light-sensitivity in the zinc sulfide.

The stability of cupric hydroxide precipitated along with other metal hydroxides was pointed out on p. 470.   The transformation, on warming, of blue cupric hydroxide into black cupric oxide is by no means the simple dehydration: $Cu(OH)_2 \rightarrow CuO + H_2O$ that is so often assumed.   The change does not occur if the cupric solution has been treated with insufficient quantities of base, or if other metal ions that are precipitable with OH^- ions are present along with the Cu^{++} ions.   The dehydration requires free $Cu(OH)_2$ and excess of OH^- ions.[202]   Probably the adsorption of alkali hydroxide or OH^- ions on the cupric hydroxide plays a decisive part.   The following mechanism may be involved.   The adsorption layer of the adsorbate consists of alkali hydroxide adsorbed on $Cu(OH)_2$ molecules.   This adsorption complex is isomeric with alkali cuprite, e.g., $Na_2[CuO_2]$, and presumably they are present as an equilibrium mixture.   Hence, there is the possibility of a local reaction on the surface of $Cu(OH)_2$ with cuprite or its ions:

$$Cu(OH)_2 + CuO_2^{--} \rightarrow Cu[CuO_2] + 2OH^-$$
(solid)   (adsorbed)
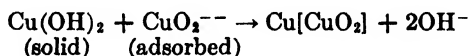
Accordingly, cupric oxide is produced with regeneration of alkali or of OH^- ions that again are susceptible of adsorption or capable of forming cuprite.   This mechanism pictures the change of $Cu(OH)_2$ into CuO as a catalytic process in which the OH^- ions adsorbed on the $Cu(OH)_2$ act as the catalyst.

In this connection it should be distinctly kept in mind that enhanced reactivity of a material does not signify that a reaction, which of itself is impossible, can thus be forced into being.   An occurrence of this kind would contravene the second law of thermodynamics.   Enhanced activity is used here in the sense of increased reaction velocity.   This result may be due to the fact that the reaction has taken a new path (as in intermediate reaction catalysis, for instance), or because molecules of a reactant have undergone a change in constitution.   Such changes in constitution can occur through passage of a molecular species into an isomeric form, or through an alteration of the molecule (deformation) that cannot be represented by a structural formula.   On the other hand, the speed of a reaction is known to depend on the concentrations of the reactants, i.e., it is subject to the law of mass action.   Since, by definition, adsorption represents an increased concentration at an interface, it might be hastily concluded that every adsorption must contribute to an increase

[202] For literature on the stability and transformation of blue cupric hydroxide see H. B. WEISER, Inorganic Colloid Chemistry, Vol. II, p. 151, New York, 1935.

in reaction velocity. The term "contribute" is stressed, because influences of other kinds, whose effects may be to retard or accelerate the reaction, are purposely disregarded in this discussion, where the influence of the change in concentration is the sole consideration. It should be remembered, first of all, that adsorption results in a localized increase in concentration which, however, is always achieved through the action of some sort of binding force. Hence, this increase in concentration is not one that can be simply compared with an increase that is secured, for instance, by merely removing solvent from a solution. It is understandable, then, that a net decrease in reactivity can result, despite a formal increase in concentration, if strong adsorptive binding forces are involved. Obviously, a retarding influence stemming from adsorptive binding will be of least import when the adsorption is weak. Even though every adsorption, because of binding, must act as a potential retardant, nevertheless, the concentration increase resulting from adsorption may be sufficient to bring about a rise in the reaction velocity. The factors influencing this state of affairs become clear if the reaction is examined with respect to the numbers of molecules of the reactants. Monomolecular reactions are known to be independent of the concentration of the consumed portion; consequently, they are not subject to influence by adsorption. A second order reaction: $A + B \rightarrow C$ is not accelerated by adsorption of A or B alone, because the probability of A meeting B is then no greater than when both molecular species are freely movable. However, the velocity of the reaction may be increased if both A and B are adsorbed. In reactions of the third order: $2A + B \rightarrow C$, an acceleration may result even if only the molecular species A is adsorbed, because the probability of B meeting two adsorbed molecules of A is greater than when they are in solution. On the other hand, the speed of this reaction will not be increased if only B is adsorbed. These two examples will suffice to demonstrate that the mere adsorption of a molecular species that appears with a molecular coefficient of 1 in an equation does not speed up a reaction. An increase in velocity is possible only when a second reactant is also adsorbed. If a reactant has a coefficient of 2 in the reaction equation its adsorption may possibly result in an increase in the reaction velocity. Reactions of higher than the second order are not common, since they usually proceed through stages that consist of lower order reactions. It seems clear, then, that the increased concentration resulting from adsorption will not play any particular part in speeding up reactions.

The influences of adsorption on the activity of the adsorbed materials doubtless are more significant than the concentration increases just discussed. All experience substantiates this statement. Whether, and

how, adsorption affects a catalyst that is acting in a homogeneous system is an interesting question.   An instance of the failure of a catalytic action because of adsorption was cited on p. 523, where it was pointed out that acids adsorbed on carbon do not invert cane sugar.· It is well known that the action of acid in inversion is a catalysis due to H^+ ions.   The reverse effect, namely, enhancement of the activity of a catalyst through adsorption, is illustrated by studies made by Elissafoff.[203]   He investigated the catalytic decomposition of hydrogen peroxide on glass powder in the presence of soluble copper salts.   Although each of these materials by itself speeds up the decomposition, the rate of decomposition when both glass powder and Cu^{++} ions are present is far greater than corresponds to an additive effect.   Probably the catalytic action of the copper is raised by its adsorption on the glass, but there is also a possibility that the simultaneous adsorption of copper and hydrogen peroxide on the glass may play a part.   The mere local accumulation of a catalyst through adsorption may likewise lead to interesting effects.   Hedges and Myers[204] found that the rate of solution of metals in hydrochloric acid is enormously increased by the addition of chloroplatinic acid.   The latter, in concentrations as low as 10^{-9}, increases the reaction velocity by more than 20% in the system: aluminum $+1$ N hydrochloric acid.   This effect is doubtless due to the production of a local element as a result of the deposition of metallic platinum on the surface of the aluminum.   However, platinum chloride is obviously also simultaneously adsorbed on the walls of the glass container in which the dissolution is proceeding.   This is proved by the fact that a glass vessel which has been used as the container for dissolving a metal in hydrochloric acid, catalyzes a second reaction of this kind, even though the vessel is thoroughly washed between the successive trials.

If the increase or decrease of the reactivity of an adsorbent or adsorbed material toward a dissolved reactant is considered from the standpoint of the equilibrium of the particular reaction in the solution, it must be stated that only the decrease in the reactivity of an adsorbed material signifies a shifting of the equilibrium.   This displacement can be so drastic as to result in the total non-occurrence of the reaction.   The diminution of the reactivity of an adsorbent does not represent an equilibrium shift since the interior of the· adsorbent has, of course, remained unaltered.   A slowing-down of the establishment of the equilibrium results only from coating the adsorbent with the adsorption layer, but this effect, likewise, can go so far that practically all reactivity is lost.   In contrast, enhanced reactivity of an adsorbed material or

[203] G. von Elissafoff, *Z. Elektrochem.* **21**, 352 (1915).

[204] E. S. Hedges and J. E. Myers, *J. Chem. Soc. (London)* **125**, 621 (1924).

adsorbent invariably means a rise in the speed of reaction without a shift of the equilibrium.

In all the cases considered thus far the adsorbent or the adsorbed material actually participates directly in the reaction. It is necessary to consider also the adsorption of a reaction product coming from a reversible reaction in which the adsorbent is not a direct participant. This condition may upset the equilibrium and, patently, the seriousness of this disturbance can be expected to increase with rising tenacity of the adsorptive binding. Examples of this are provided by hydrolytic adsorptions (see p. 506) in which, quite generally, the preferential adsorption of true or colloidally dissolved hydrolysis products results in a shift of the equilibrium in the direction of more extensive hydrolysis. Fundamentally, it makes no difference, with respect to the shifting of an equilibrium through adsorption of one of the products of a reversible reaction, whether the adsorbent is added as a fine powder to the reaction system or whether the adsorbent is formed within the medium of the equilibrium reaction. It is only natural to expect that the latter circumstance will lead to a more extensive disturbance of the equilibrium, since a physical condition characterized by a very great specific surface is invariably traversed whenever a solid phase is produced from solution. Many of the cases of induced precipitation cited in Chapter V can be considered from these viewpoints. For instance, the hydrolysis of iron-containing titanium solutions does not produce white $TiO_2 \cdot aq$, but a yellow product. The reason is that the titanic acid, during its precipitation, adsorbs the basic hydrolysis products of the ferric solution and thus promotes the hydrolysis of the ferric salt. Other examples are found among induced precipitations of sulfides in which the precipitation of a second sulfide brings about the deposition of considerable amounts of certain other sulfides at pH values at which the latter sulfides normally do not come down at all. In such reaction anomalies, the equilibrium of the secondary precipitation may be shifted because of adsorption on products of a primary precipitation. Equilibrium shifts that are not only interesting but also of value in analysis may be brought about by adding tannin to solutions of readily hydrolyzable salts. Quantitative precipitations of the metal often results. These precipitations are due to the union of basic hydrolysis products with colloidally dispersed tannin particles to form acid-resistant adsorption compounds or systems. This topic will be discussed later.

The statements in this section concerning the increased reactivity of adsorbed materials can well be supplemented by a reference to the behavior of gases adsorbed on solids. In Chapter V it was pointed out that hydrogen and carbon monoxide in contact with platinum metals

exert reducing actions which are not usual for the molecules of these gases or that otherwise proceed extremely slowly. Analytical use has been made of these findings. In such cases, the activation is due to the adsorption of the hydrogen or carbon monoxide or is initiated by the adsorption. It should be emphasized that an adsorption activation of hydrogen is not restricted to the surface of platinum metals. Reyerson and his associates[204a] found that hydrogen adsorbed on silica gel exhibits reducing actions that are not brought about by gaseous hydrogen at all, or else only slowly: Au^{III}, Pt^{II} and Pd^{II} salts are reduced to the respective metals, and Cu^{II} to Cu^{I}. It is particularly interesting that $[Cu(NH_3)_4]^{++}$ and $[Ni(NH_3)_4]^{++}$ adsorbed on silica gel are reduced to the metal by the activated hydrogen. Accordingly, in these instances also, adsorption of the ammine ions has brought about their activation.

It is quite remarkable that adsorbed oxygen effects more powerful or, more correctly, more rapid oxidizing actions than the free gas. This has been demonstrated with solutions of autoxidizable salts, which undergo extensive oxidation if they are shaken in contact with charcoal that contains air.[204b] Since carbon is a strong reducing agent and since solutions of salts of noble metals (Ag, Au, Pt, Pd) are readily reduced to the metal, it would appear logical to expect that solutions of autoxidizable salts would be stabilized by suspended carbon. The fact that the reverse is true, demonstrates that oxygen adsorbed on carbon is highly activated. The findings of Feitnecht,[204c] which are discussed in Chapter XI, show that adsorption and the related activation of oxygen play a decisive role in the autoxidation of the insoluble hydroxides of Fe^{II}, Mn^{II}, Co^{II}, and Ce^{III} in contact with air. Perhaps, the same considerations hold for the relatively strong autoxidation of freshly precipitated sulfides of the ammonium sulfide group. The activation of a gaseous reactant may be involved when acetylene acts on water solutions of palladium or osmium salts. It is well known that yellow-brown palladium acetylide, PdC_2, can be quantitavely precipitated by passing acetylene into an acidified palladous solution. The action of this gas on osmium salts is slow; reduction occurs, but the deposition of the resulting metal is not complete. Makowa,[204d] however, made the interesting discovery that passage of acetylene through palladous solutions containing osmium also, results not only in the precipitation of

[204a] M. Latshaw and L. H. Reyerson, *J. Am. Chem. Soc.* **47**, 610 (1925); G. W. Smith and L. H. Reyerson, *ibid.* **52**, 2584 (1930).

[204b] F. Feigl, *Z. anorg. allgem. Chem.* **119**, 305 (1921); H. Freundlich and A. H. Fischer, *Z. phys. Chem.* **114**, 413 (1925).

[204c] W. Feitknecht, *Helv. chim. Acta* **24**, 672, 676, 694 (1941).

[204d] O. Makowa, *Z. anal. Chem.* **46**, 145 (1907).

PdC₂, but, after prolonged action, all of the osmium comes down. At first glance, this would seem to be an instance of induced precipitation. However, it must be remembered that there are two kinds of induced precipitation. In one of these, a precipitation, which, by itself, does not take place at all or only slowly, is forced to occur by the production of another precipitate, in such manner that the induced and the inducing precipitate are identical with respect to their cationic or anionic component. (Compare the examples of induced precipitations of sulfides and oxides cited in Chapter V.) Another, much less common, form of induced precipitation occurs when a hydrosol is coagulated by a precipitate. [Compare p. 473, the induced coagulation of Cr_2O_3 hydrosol by the precipitation of HgS.] The induction of the redox reaction between acetylene and osmium through the precipitation of palladium acetylide obviously does not fall within the bounds of either of the categories of induced precipitation. A plausible explanation of the reaction anomaly observed by Makowa is provided by assuming that acetylene is adsorbed on PdC_2 and thus activated.

THE ADSORPTION OF DYES

The behavior of organic dyes must be given a prominent place in discussions of the adsorption phenomena that have analytical importance. Many colloidal studies showed long ago that dyes are taken up, in conformity with an adsorption isotherm, by charcoal, silk, and other substrates. The analyst is especially interested in the corresponding action of inorganic materials that are of salt or oxide nature, since it has been found that such substances frequently are tinted or changed in color by taking up dyes. In many cases there is a characteristic color change which can be employed by the chemist for analytical purposes. The tinting of water-insoluble metal salts and oxides by aqueous solutions of dyes, which frequently cannot then be washed out with water, doubtless involves adsorption phenomena. The bulk of the solid phase remains unaltered in such cases and hence only its surface portions are involved in the tinting process. Accordingly, it is logical to assume that fundamentally all of the types of adsorption which were listed in the preceding section may play a role here. These include: (a) adsorption of undissociated dye molecules; (b) exchange for dye ions of lattice ions of the solid phase; (c) adsorption of dye ions on salt and oxide particles; (d) exchange for dye ions of ions previously adsorbed on the particles.

The analytically interesting effects of tinting precipitates, either recently formed or in *statu nascendi*, obviously involves, for the most part, an exchange of ions which have been adsorbed on the precipitates. The reason is that precipitates, because of their production from aqueous

solution, never conform absolutely to the composition stated by the formula; they invariably are in adsorption equilibrium with the ions present. The ions adsorbed on a precipitate may be identical with an ionic species which is producing the precipitate, but along with this species, or even predominantly, there may be adsorption of other varieties of ions, especially H^+ or OH^- ions, in case the precipitation takes place from acid or basic solution. When speaking of adsorbed ions it is necessary constantly to keep in mind both the charge-determining ions, *i.e.*, those that are fixed directly on the surface of the sol or gel particles, and also such portions of the corresponding counter ions (see p. 507) which are situated in the immediate vicinity of the adsorbing surface and which, therefore, are close to the charge-determining ions.

Fundamental observations on the tinting of salts, which only later were brought into their proper connection with adsorption, were made by Hübl.[205] He found that fluorescein dyes show characteristic color changes on silver halides, and also that the observed change depends on whether the particular halide was prepared in the presence of excess silver or of halide salt. The equally fundamental findings of Lottermoser (see p. 452) proved that silver halides can be peptized by either silver or halide ions and thus, by virtue of the adsorbed Ag^+ or Hal^- ions, acquire either a positive or a negative charge. It seemed obvious that the findings of Hübl and of Lottermoser must be related. , This relation was disclosed by the classical experimental studies and theoretical discussions published by Fajans and his associates.[206] According to him, the adsorption of dye on silver halides should be regarded as a secondary process that follows the primary adsorption of silver or halide ions on silver halide particles. In fact, the adsorption of silver ions promotes the adsorption of dye anions, and the adsorption of halide ions favors the adsorption of dye cations. Such adsorbed dye anions can be displaced by the addition of halide ions and, conversely, adsorbed dye cations can be expelled by adding silver ions. The color changes, first observed by Hübl, accompany the adsorption of dye ions. Fajans ascribes the color change to a deformation of the dye ions, and holds the electrical fields of the primary adsorbed ions responsible for this deformation. The secondary adsorption of the dye does not take place, for instance, because silver or halide ions are replaced by the oppositely charged dye ions, but rather, according to Verwey,[207] because the dye ions take the place of

[205] A. v. Hübl, Eder's *Jahrb. Photographie* **1894**, p. 189.

[206] K. Fajans and O. Hassel, *Z. Elektrochem.* **29**, 495 (1923); K. Fajans and W. Steiner, *Z. physik. Chem.* **125**, 309 (1927); K. Fajans and H. Wolf, *Z. anorg. allgem. Chem.* **137**, 221 (1924); O. Hassel, *Kolloid-Z.* **34**, 304 (1924).

[207] E. J. Verwey, *Kolloid-Z.* **72**, 187 (1935).

those counter ions which belong, respectively, to the silver or halide ions. For example, if the counter ion of an adsorbed silver ion is a nitrate ion, the latter is replaced by a dye anion. Conversely, if an alkali ion is functioning as the counter ion of an adsorbed halide ion, its place is taken over by a dye cation. Accordingly, in both cases, inorganic counter ions are exchanged for dye ions. This signifies, in a formal sense, or, in the opinion of the present writer, the actual production of dye salts in the adsorption layer, and the binding of these colored salts to the silver halide. This process may well involve a certain measure of coordinative binding of the dye salts, somewhat along the lines encountered in double salts. Any exchange of counter ions must, of course, cease at the isoelectric point. The latter may coincide with the equivalence point of a silver halide precipitation. However, the isoelectric point of a precipitation reaction can be shifted away from its equivalence point. This occurs, for instance, in the precipitation of silver iodide, which avidly adsorbs iodide ions. If it is desired to detect the equivalence point by means of a color change, it is necessary to compensate for this shift by balancing the extraordinary adsorption of iodide ions by a particularly strong adsorption of dye ions. Under such conditions there no longer is a mere exchange of counter ions, but rather an additional adsorption of dye ions is an integral part of the indicator action.

The very fitting designation "adsorption indicators" was proposed by Kolthoff[208] for dyes which, because of adsorption, exhibit a characteristic color change at the equivalence point of a precipitation reaction. The following instance illustrates the adsorption indicator action of acid and basic dyes:[209] "About 3 mg. of the sodium salt of eosin is added to a liter of distilled water. The salt is dissociated and partially hydrolyzed imparting to the solution a greenish fluorescence and a yellowish red color in transmitted light. The addition of 2 ml. of 0.1 N AgNO$_3$ causes no appreciable color change since the solubility product of silver eosinate is not exceeded. On adding 0.5 ml. of 0.1 N alkali bromide, an intense color change to red or red-violet occurs and the fluorescence disappears. The highly dispersed silver bromide adsorbs silver ions and, simultaneously, an equivalent amount of eosin ions, which are deformed, the process causing a marked change in color. On further addition of bromide, more silver bromide results and the color deepens until the equivalence point is passed, whereupon the excess bromide ions displace the adsorbed eosin ions, which return to the solution. The silver bromide particles are

[208] I. M. KOLTHOFF, Volumetric Analysis (translated by N. H. Furman), Vol. I, p. 111. New York, 1928.

[209] Quoted from H. B. WEISER, Inorganic Colloid Chemistry, Vol. III, p. 132. New York, 1938.

decolorized thereby, and the solution takes on its original color and fluorescence. The color change is completely reversible.

"If a basic dye such as Rhodamine 6G is substituted for eosin, the process is the reverse of the above. In the presence of excess silver ions, these are adsorbed primarily and prevent the adsorption of the dye cation; but as soon as a slight excess of bromide is present, the latter ions are adsorbed and attract an equivalent amount of dye cations which give an intense red color to the silver bromide suspension."

The use of adsorption indicators is not limited to titrations that involve solutions of silver salts. The endpoint of many other precipitation reactions can be indicated by the use of small amounts of certain acid or basic dyes. At the instant of equivalence they characteristically tint the still suspended precipitate, or they color the precipitate just before this point is reached and then go back into solution with a different color, immediately after the equivalence point is passed. It is beyond the province of this text to discuss the numerous cases in which adsorption indicators have been applied satisfactorily.[210]

The discovery and application of adsorption indicators and the elucidation of their *modus operandi* demonstrate the definite analytical significance of surface effects. However, the dependence of the indicator action on surface effects also sets a limit to the range of usefulness of adsorption indicators. The reason why every acid or basic dye cannot be used to indicate the completion of precipitation reactions is likewise to be sought in this dependence on surface effects. Obviously, the action depends on all the factors which are connected with the development and continuing existence of the surfaces of solid phases. Hence, such factors as: the nature of the precipitation reactions and their products, and also the maintaining of definite reaction conditions (concentration, pH, nature of cosolutes, *etc.*) play decisive roles.[211] It must also be noted that dyes can be taken up in any of the various ways cited on p. 530, and the desired endpoint color change may thus be concealed or prevented.

A tinting along the lines of the action of adsorption indicators seems to be especially possible in the case of crystalline precipitates. It is characteristic of this type of dyestuff adsorption that it can be reversed by lattice ions of the same sign. In other words, adsorbed dye cations

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[210] Excellent and extensive discussions of the use of adsorption indicators are given in: I. M. KOLTHOFF and V. A. STENGER, Volumetric Analysis, 2nd. rev. ed., Vol. I, p. 102. New York, 1942; Vol. II, p. 245. New York, 1947. K. FAJANS in Newer Methods of Volumetric Analysis (edited by W. Böttger) (translated by R. E. Oesper), New York, 1938. Shorter presentations may be found in the standard textbooks of quantitative analysis.

[211] I. M. KOLTHOFF, *Chem. Revs.* **16**, 87 (1935).

(anions) are expelled by the addition of cations (anions) of the lattice of the precipitate. The taking-up of dyestuff ions by precipitates in the presence of an excess of precipitating ions corresponds to an induced precipitation of dyestuff salts. Hence, it can be expected that colored instead of colorless precipitates will be produced when the precipitation is carried out in the presence of dyestuff ions which are susceptible to an induced precipitation. In fact, Fischer[211a] showed that red, instead of the normally colorless, $LaF_3 \cdot 3H_2O$ is thrown down when La^{+++} ions are added to an acetic acid solution of fluoride that also contains eosin. Minute quantities of fluoride, that are too slight to be revealed by the precipitation of pure LaF_3, are readily detected by this means. Accordingly, the possibility of enhancing, through dyestuff adsorption, the sensitivity of detection reactions producing crystalline precipitates should be studied.

Hydrous metal oxides frequently remove dyes irreversibly from aqueous solutions. This fact is of analytical interest and is put to use when the solution color of the dye differs from that of the tinted oxide. The taking up of dyes by hydrous oxides has been used for many years since it is the basis of mordant dyeing of textiles. The so-called metal mordants are prepared by impregnating the cloth or fibers with finely divided metal oxides, a process that in itself is a kind of adsorption. Through the mordants it is possible to fix dyes on fibers that normally are not capable of taking up the particular dye irreversibly. The term "color lake," which was originally used to designate such combinations, is now applied to the products formed by coloring mordants, in the absence of textile fibers, by means of suitable (mordant) dyes.

It was long supposed that color lakes were actual compounds, resulting from chemical combinations of dyes and oxides. This assumption was based primarily on observations that acid dyes, in which the anion is the colored constituent, are taken up only by basic oxides, and basic dyes, whose cation is the colored component, are fixed only by acidic oxides.[212] For example, hydrous aluminum oxide takes up the acid dye alizarin, and it was assumed that aluminum alizarinate results. Biltz[213] was the first to dispute the supposition that true alizarinates are invariably formed when hydrous oxides are colored by means of this acid dye. He showed that the quantity of alizarin taken up by chromium oxyhydrate, which is strikingly active, varies continuously with the concentration of the dye in the bath, and, in fact, follows an adsorption isotherm.

[211a] J. Fischer, Z. anal. Chem. 104, 344 (1936).

[212] Compare H. Rheinboldt, and E. Wedekind, Kolloidchem. Beihefte 17, 115 (1923).

[213] W. Biltz, Ber. 38, 443 (1905).

The findings of Bull and Adams[214] and of Williamson[215] likewise support the lack of production of an alizarinate. They found that washed precipitates of hydrous oxides are intensely colored when shaken with the dye solution, but nevertheless no sodium hydroxide is set free as would be expected if OH groups had been replaced by alizarin radicals. They consequently assume that sodium alizarinate is adsorbed as such, that is, in its molecular form.

Important insights into the processes that play a part when hydrous oxides of iron, chromium, and aluminum form alizarin lakes were provided by the careful studies of Weiser and his students.[216] They took into account also the effect on lake formation of such factors as the aging of the oxides, pH, and the nature of the cosolutes in the dye solution. Their findings left no doubt that the coloring of basic mordants is adsorptive in nature and does not depend on the formation of definite compounds. Several of their findings are especially informative. It was found that, after a 0.01 N sodium alizarinate solution is decolorized by means of a Cr_2O_3 hydrosol which then flocculates with production of a yellow-brown chrome-alizarin lake, about 85% of the original sodium remains in the solution. Similar results were obtained when Al_2O_3 and Fe_2O_3 hydrosols were flocculated by sodium alizarinate. A ferric oxide sol, prepared by hydrolysis of ferric chloride, purified by dialysis, and then stabilized by adsorption of hydrochloric acid (H^+ ions as charge-determining ionic species), was coagulated by means of sodium alizarinate. The resulting clear liquid contained a quantity of sodium chloride that corresponded exactly to the hydrochloric acid content of the sol. Analogous results were obtained in trials with an alumina sol stabilized with hydrochloric alone.[217]

These experiments on lake-formation when oxide sols are coagulated prove that a molecular adsorption of sodium alizarinate does not occur. Rather, inorganic anions adsorbed on the oxide particles are exchanged for alizarin anions. The adsorption of alizarin ions is also indicated by the fact that gels of hydrous oxides take up this dye at rates, and to extents, which are markedly influenced by the other ions that are present in the alizarin solution. The adsorption of alizarin ions is increased when strongly adsorbable cations are present in the dye bath, while strongly adsorbable anions lower the rate and extent of the adsorption of

[214] A. W. BULL and J. R. ADAMS, *J. Phys. Chem.* **25**, 660 (1921).

[215] F. S. WILLIAMSON, *J. Phys. Chem.* **28**, 891 (1924).

[216] A comprehensive presentation of these studies is given in H. B. WEISER, Inorganic Colloid Chemistry, Vol. II, Chapter XVI. New York, 1938.

[217] It is also possible in the case of Fe_2O_3·aq and Al_2O_3·aq that the charge is not due to adsorbed H^+ ions, but rather to a partial dissociation of the surface molecules of $Fe(OH)_3$ and $Al(OH)_3$.

alizarin ions correspondingly. Accordingly, the effect here is similar to that discussed in connection with the action of adsorption indicators, in which an exchange of counter ions plays an important role. Hence, although it is certain that alizarin ions combine with sol and gel particles *via* an ion exchange, nevertheless, other types of adsorption must also be taken into account in the production of alizarin lakes. This is shown clearly by the findings of Weiser in his study of the alizarin lakes formed with fibrous alumina. The latter is a variety of $Al_2O_3 \cdot aq$ produced by treating amalgamated aluminum with water. In contrast to precipitated alumina it is free of adsorbed ions. It was found that this material forms red lakes with alcohol solutions of alizarin as well as with water or alcohol solutions of sodium alizarinate. No sodium hydroxide was detected in the filtrate after fibrous alumina produced a lake with sodium alizarinate. Since, in this case, there can be no question of an exchange of adsorbed ions, Weiser assumes that alizarinate ions as well as sodium ions are adsorbed on the alumina; the former on Al atoms, and the latter on O atoms of the Al_2O_3 surface. Hence, this presents the remarkable case in which different parts of the surface function differently. The present writer believes that the divided adsorption postulated by Weiser is in reality nothing other than a salt-like binding of the ionic species of the sodium alizarinate. In other words, the alizarin ions are held by Al atoms in the same manner as in aluminum alizarinate, and the sodium ions are bound as in sodium aluminate. Similarly, the lake-production by the action of fibrous alumina with an alcohol solution of alizarin is viewed as a salt-like binding of the alizarin radical. This concept does not abandon an adsorption theory of lake formation, because it can be brought into agreement with the requirement that the binding of the alizarin must not lead to the production of a new phase, *i.e.*, of a definite aluminum alizarinate. In the preceding sections it was repeatedly pointed out that a particular type of binding between the adsorbent and the adsorbed material is not the characteristic feature of an adsorption, but rather that the retention of a material on the surface of an adsorbent is the sole characteristic criterion. It is quite easy to see that a salt-like binding of alizarin radicals (Aliz) on an aluminum atom by no means need be synonymous with the formation of a definite aluminum alizarinate as represented by the formula $Al(Aliz)_3$. Alizarin invariably functions as a monobasic acid when it forms an aluminum salt. Accordingly, if only a single OH group of the $Al(OH)_3$ molecule is replaced by an alizarin radical, this replacement can occur on the $Al(OH)_3$ molecules situated on the surface of alumina without detaching them from the original phase association. Such surface reactions are represented here schematically; (a) and (b) represent the formation of a lake with alizarin and sodium alizarinate, respectively:

$$[Al(OH)_3]_x + HAliz \rightarrow [Al(OH)_3]_{x-1}\cdot Al\overset{\displaystyle Aliz}{\underset{\displaystyle OH}{\diagup}}OH + H_2O \qquad (a)$$

$$[Al(OH)_3]_x + NaAliz \rightarrow [Al(OH)_3]_{x-1}\cdot Al\overset{\displaystyle Aliz}{\underset{\displaystyle ONa}{\diagup}}OH + H_2O \qquad (b)$$
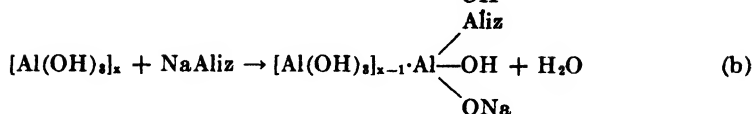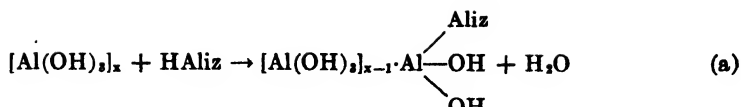
These reaction schemes are intended to show that alizarin is bound on the surface of Al(OH)$_3$ in the same manner as in aluminum alizarinate. However, three alizarin radicals never combine with one aluminum atom in the surface as would be required to initiate the development of a new phase. Instead, there is only a partial alizarination, a fact that can also be expressed by saying that a basic alizarinate is formed on the surface. The ratio of alizarin to the total aluminum in the products of the foregoing reactions will always be less than 3:1. The deviation from this ratio will depend on the extent of the specific surface of the aluminum hydroxide on which the salt-formation occurs, and on the ions that may have been adsorbed there. As will be pointed out later, combinations of materials like those produced by the irreversible adsorption of alizarin are called "adsorption compounds."

The tenacious surface binding of alizarin is related to the fact that it is a compound not only acidic in nature but, in addition, capable of coordinative linkage because it possesses a CO group in the *peri* position to an OH group. The red, water-insoluble aluminum alizarinate, as shown by (I), is an inner complex salt. Möhlau[218] prepared this compound by reacting aluminum salts with mono potassium alizarinate. In analogous fashion, Atack[219] produced the compound (II) from the sodium salt of alizarin sulfonic acid. This product likewise is red and insoluble in water. The close resemblance between these two aluminum salts in color and solubility justifies the assumption that they are similarly constituted as shown in (I) and (II):

(I)   (II)
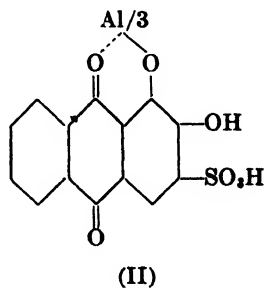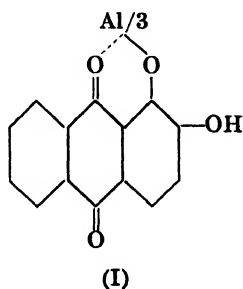
[218] A. Möhlau, *Ber.* **46**, 443 (1913).
[219] F. W. Atack, *J. Soc. Chem. Ind.* **34**, 936 (1915).

The aluminum lakes of alizarin and alizarin sulfonic acid, that can be prepared by tinting aluminum hydroxide, are not so intensely red as the corresponding pure aluminum salts, but among themselves the color lakes are approximately alike in color.   Consequently, it may be assumed that the alizarin and the alizarin sulfonic acid are held on the surface of the alumina by the same type of binding, and that the inner complex aluminum binding shown in (I) and (II) can be regarded as the color-conferring factor in the lake formation.   Despite the identity in the type of binding forces holding the alizarin molecules, it is not permissible, however, to regard formation of lakes as identical with the production of inner complex salts in a separate phase.   The necessity of distinguishing between these two processes becomes evident when the properties of the aluminum alizarinates isolated by Möhlau (*loc. cit.*) are compared with those of aluminum alizarin lakes, precipitated by treating aluminum salt solutions with ammoniacal solutions of alizarin.   The aluminum alizarinate is resistant to 1 N hydrochloric acid and dissolves in ammonia (compare p. 202), whereas the lake is decomposed by much weaker hydrochloric acid and is stable against ammonium hydroxide.   Hence, the widespread statement in the analytical literature that aluminum-alizarin lake is to be regarded as an inner complex aluminum alizarinate is incorrect.

The tinting of alumina by alizarin has been discussed here in considerable detail because it is a model example of lake-formation.   Furthermore, it is now clear that adsorptive processes of various kinds must be taken into account here.   When the production of lakes is used in analytical practice, sometimes previously formed hydrous oxides are tinted, but the more common procedure is to treat solutions of metal salts with alkaline solutions of a lake-forming dye.   It must then be remembered that the occurrences, which were discussed as elementary processes in the formation of aluminum alizarin lakes, proceed concurrently and to different extents, depending on the prevailing experimental conditions and the nature of the lake-forming components.   If alkaline solutions of a lake-former are employed as reactants, the extensive surface of hydrous oxides *in statu nascendi* will be an important factor. Under such circumstances, consideration must be given to the possibility of decided adsorption of dyes or, in some cases, even of the production of definite, water-insoluble metal salts of the particular dye.   It is not merely a chance coincidence that all lake-forming acid dyes are so constituted that they are capable of forming inner complex salts, and accordingly possess groups that are suitable for the production of both principal valence linkings and auxiliary bindings.   Werner,[220] in a study that is one of the classics in the literature of complex chemistry, was the

[220] A. WERNER, *Ber.* **41**, 1062 (1908).

first to draw attention to this fact. He showed that the principle of mordant dyeing, *i.e.*, the production of color by fixing dyes irreversibly on textiles impregnated with metal oxides, is also satisfied by those colorless organic compounds which are capable of producing colored inner complex salts with the metal contained in the oxide. His conclusion that lake-formation is identical with the formation of inner complex salts can, however, no longer be sustained in this all-embracing form. The formation of such definite inner complex salts as a separate phase, which obviously was what Werner meant, can occur as the extreme case in lake-formation. In general, however, the conversion of oxides of di- and higher valent metals to inner complex dye salts stops at the surface of the oxide and does not proceed to completion. It is precisely this limitation and the consequent prevention of the development of a new phase which characterizes lake-formation as a typical phenomenon of adsorption. The concept set forth here regarding the formation of lakes accordingly connects the correct fundamental idea advanced by Werner with the experimentally demonstated fact of the adsorptive taking up of the dye advanced by Weiser.

Table XXIV presents a survey of lake-forming organic compounds which are used, in alkaline solution, as analytical reagents.[221] All dyestuffs, which function as lake-formers in the alkaline pH range, contain characteristic atomic groups, of which several types are shown here. (Certain lake-formers not named in Table XXIV are also included.)
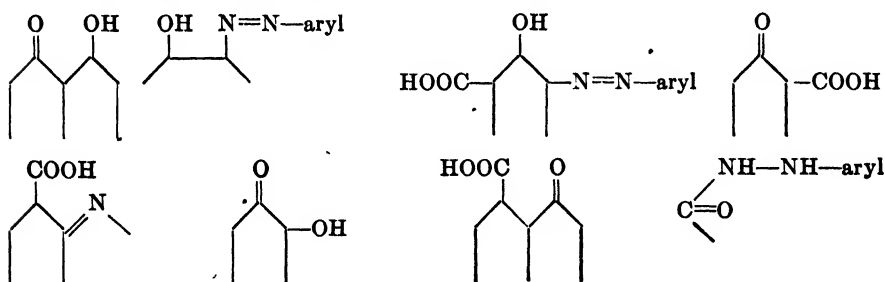
Accordingly, this discussion concerns acid dyes, containing acidic H atoms and coordinatable O- and N- atoms so situated that, when the salt is formed, ring closures are possible through the participation of principal and auxiliary valences. It seems natural to designate such dyestuffs as inner complex-formers. However, it should be noted that the presence of such atomic groupings is by no means a *de facto* guarantee that insoluble inner complex salts will be formed. The precipitation of a salt requires

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[221] F. J. Welcher, *op. cit.*, Vol. IV, Chapters 14–16 gives an extensive survey of color lake reactions employed in analytical chemistry.

that the solubility product be exceeded and its value doubtless depends on factors beyond the mere replaceability of acidic H atoms by metal atoms. Important roles are played here by other components of the molecule, *e.g.*, hydrophilic and hydrophobic groups. These are the determining factors with regard to the tendency to form a separate solid lattice, and for the tendency to pass into the water phase. The following review proves that it is not permissible to predict the formation of insoluble formula-pure inner complex salts from the constitution of lake-forming dyes. Among about 25 dyes, which produce color lakes with aluminum, inner complex aluminum salts have actually been isolated only in three cases. These are: alizarin (Möhlau, *loc. cit.*), alizarinsulfonic acid (Atack, *loc. cit.*), and morin,[221a] and then only under conditions which are not those obtaining during the analytical production of the respective lakes. Among the much larger number of dyes, which form lakes with Be, Cd, Zn, Mg, *etc.*, not a single instance has been reported of the isolation of a pure metal salt. Therefore, dyestuffs, whose constitution provides them with an innate ability to form inner complex salts, actually show little effective tendency to produce such salts. Furthermore, it is surely not mere chance that the formation- and existence-range of metal color lakes always coincide with those of the respective metal oxides (hydroxides) in the gel or sol form. This clearly signifies that solid particles of the oxide (hydroxide), rather than metal ions, function as reactants in the formation of lakes, and that the reaction product is not formed as a separate phase, but remains in the phase domain of the solid. This corresponds to the reaction picture suggested for the aluminum-alizarin lake. It appears that, in the lakes, because of the steric interference of the surface molecules, there results a general reaction, involving principal and inner complex auxiliary valence bindings, which cannot be realized through the reaction of freely movable metal ions with dyestuff anions.

The foregoing comments assume that the simultaneous principal and auxiliary valence binding of dyestuffs to metal atoms on the surface of oxides (hydroxides) is essential to lake-formation. However, it is possible that dyestuffs are fixed solely by coordinative bonding, and this would then correspond to an addition adsorption. In the spirit of the interpretation given here, metal color lakes are adsorption compounds (compare the next section) of dyestuffs with metal oxides (hydroxides), whose production involves the participation of coordinative bindings.[221b] If

[221a] E. SCHANTL, *Mikrochemie* **2**, 174 (1924).

[221b] Compare F. FEIGL and H. W. ZOCHER, Contributions to Chemical Adsorption. *J. Colloid Science* (in press).

the latter is emphasized, metal color lakes should be viewed as complex compounds of stoichiometrically undefined composition.[221c]

Color lakes have considerable analytical importance because their formation is selective in many instances and often the selectivity can be enhanced by suitable measures. In addition, the formation of lakes can be included among the most sensitive of known reactions. Atack,[222] in his study of the Al-alizarin lake, was the first to demonstrate the potentialities of these systems as analytical aids. He showed that the lake not only provides a sensitive test for aluminum[223] but also serves in the quantitative determination of this element. A review of the literature reveals that only after this pioneer study, lake-producing reactions were introduced into general analytical practice. With respect to the analytical employment of lake-forming dyes, it is important to note that, despite the low water-solubility of color lakes, they nevertheless readily form colloidal dispersions (hydrosols). Weiser observed that a flocculation is the first stage when an alizarinate acts on oxide sols, and further addition of the alizarinate then brings about a peptization, which is accompanied by a reversal of the charge of the sol particles. This succession of events is often observed when lakes are formed in very dilute solutions of metal salts. Colloidal solutions displaying the color of the lake form first, and only after long standing does the lake separate in flocks. Color lakes can be easily preserved in the colloidal condition by means of organic protective colloids. This maintenance of the sol condition is the basis of colorimetric determinations, because, with small amounts of the color lake and an excess of the reagent, there is a linear relation between extinction and metal content. When the amount of lake-forming hydroxide exceeds certain values, the quantity of dye adsorbed is not proportional but decreases markedly; the extinction-concentration curve then tends to run parallel with the concentration axis. It should be noted that the color intensity of a colloidally dispersed color lake can be affected by the cosolutes present, even though they, of themselves, do not react with the lake-forming dye. For instance, Otto

[221c] A new class of lakes produced solely by coordination of dyes with Pd(CN)₂ was recently observed: cf. p. 669.

[222] F. W. ATACK, *J. Soc. Chem. Ind.* **34**, 936 (1915).

[223] The writer wishes here to pay tribute to his first collaborator, Mrs. R. Stern, who worked with him in Vienna in 1916. Because of the war no foreign periodicals were than available and, hence, she had no knowledge of the work of Atack. Quite independent of him, she discovered that alizarin is a very excellent spot test reagent for aluminum. This aluminum reaction and the equally extraordinarily sensitive manganese-benzidine reaction (see p. 332) were described in the first extensive paper that appeared on spot tests [(F. FEIGL and R. STERN, *Z. anal. Chem.* **60**, 1 (1921)].

TABLE XXIV

Dyestuff	Color in basic solution	In basic solution tints
Alkannin[a]	blue	$MgCO_3$......blue violet $CaCO_3$...........blue $SrCO_3$............blue $Al(OH)_3$..........blue
Azo blue[b]	pink	$Mg(OH)_2$........violet
Carminic acid[c]	red	$Pb(OH)_2$...... ..violet
Congo corinth[d]	red	$Mg(OH)_2$.........violet $Co(OH)_2$.........violet $Ni(OH)_2$..... ...violet
Curcumin[e]	yellow brown	$Be(OH)_2$.....red orange $Mg(OH)_2$.. red orange
Diamine Pure Blue[f]	blue violet	$Mg(OH)_2$... ......blue
1,2-Diaminoanthraquinone-3-sulfonic acid[g]	red violet	$Cu(OH)_2$..... ....blue
Diphenylcarbazide[h]	red	$Mg(OH)_2$.. blue violet $Cd(OH)_2$........violet
Gallocyanine[c]	blue violet	$Pb(OH)_2$....... violet
Naphthazarin[i]	blue	$Mg(OH)_2$..........blue $Be(OH)_2$........violet
p-Nitrobenzeneazoresorcinol[j]	red violet	$Mg(OH)_2$. ....blue
p-Nitrodiazoaminoazobenzene[k]	violet	$Cd(OH)_2$....bright pink $Mg(OH)_2$... ......blue
Titan yellow[l]	yellow brown	$Mg(OH)_2$..........red
Quinalizarin[m]	red violet	$Mg(OH)_2$.........blue $Be(OH)_2$..........blue $Ga(OH)_3$......amethyst Hydroxides of Zr, Th, La, Ce.....blue

[a] F. Eisenlohr, Ber. 53, 1476 (1920).

[b] E. Eegriwe, Z. anal. Chem. 76, 354 (1929).

[c] F. Pavelka, Mikrochemie 7, 307 (1929); 8, 395 (1930).

[d] I. M. Kolthoff, Mikrochemie, Emich Festschrift, 188 (1930).

[e] I. M. Kolthoff, J. Am. Chem. Soc. 50, 393 (1928).

[f] E. Eegriwe, Z. anal. Chem. 76, 354 (1929).

[g] R. Uhlenhuth, Chem. Ztg. 34, 887 (1910); J. V. Dubsky and V. Bencko, Z. anal. Chem. 94, 79 (1923); H. E. Ballaban, Mikrochemie ver. Mikrochim. Acta 27, 57 (1939).

[h] F. Feigl, Z. anal. Chem. 72, 773 (1927); 74, 399 (1928).

[i] J. V. Dubsky and E. Krametz, Mikrochemie 20, 57 (1936).

[j] K. Suitsu and K. Okuma, J. Soc. Chem. Ind. Japan 29, 132 (1926).

[k] F. P. Dwyer, Australian Chem. Inst. J. Proc. 3, 184 (1936); 4, 26 (1937); 5, 149, 197 (1938).

[l] I. M. Kolthoff, Chem. Weekblad 24, 254 (1927); J. Am. Pharm. Assoc. 17, 360 (1928).

[m] F. L. Hahn and coworkers, Ber. 57, 1394 (1924); for further literature compare F. J. Welcher, Organic Analytical Reagents, Vol. IV, p. 467. N. Y., 1948.

and Otto[224] observed that the color intensity of the magnesium-Titan yellow lake is greatly lessened by even traces of aluminum or small amounts of tin. In this case, magnesium hydroxide obviously strongly adsorbs aluminate or stannate and thus decreases the adsorption of Titan yellow. If the complicating effect of cosolutes is not involved, it may be taken as a guiding principle that lakes invariably form within the pH range of the precipitation of the lake-forming oxide, and are resistant within this range. (Exceptions are discussed on p. 560.) Therefore Table XXIV, which contains examples of lake-formation in basic media, could not include the aluminum-alizarin lake, because the existence range of this lake lies between pH 4–8. The aluminum lake does not form in a basic medium and, if produced under other conditions, is decomposed by alkali hydroxides. To form this red lake, it is necessary to treat a solution of an aluminum salt with an ammoniacal solution of alizarin and then acidify the violet mixture with acetic acid. Red aluminum alizarin lake and yellow alizarin acid result. The relation of the stability of the lakes and the existence-range of the lake-forming oxides is quite apparent from the findings of Fischer.[225] He studied the action of bromine water on solutions of quinalizarin and on suspensions of its magnesium and beryllium lakes. The violet ammoniacal or caustic alkali solutions of quinalizarin are decolorized by bromine water because it oxidatively destroys the dye. Caustic alkali suspensions of the magnesium lake are resistant to bromine water, whereas it is destroyed by this reagent if suspended in ammoniacal solutions of ammonium salts. Exactly the reverse is true of the beryllium lake. It is stable in ammoniacal solutions of ammonium salts and is destroyed when suspended in caustic alkali. This divergent behavior is entirely in line with the stability of magnesium hydroxide in caustic alkali and its solubility in ammonia in the presence of ammonium salts. Correspondingly, beryllium hydroxide is stable in ammonia and dissolves in caustic alkalies to form beryllates. Fischer used this divergent behavior toward bromine water to distinguish between these blue magnesium and beryllium lakes of quinalizarin. Since many dyes are subject to destructive oxidation, it is quite possible that the varying degrees of resistance of dyes in color lakes can be utilized in still other cases to increase the selectivity of color lake reactions. No comparative experiments along this line have been published. The studies by Ackerman[226] should be noted in this connection. He found that color lakes, in general, are more light-stable than their respective dyes when alone, and that the light-stability rises

[224] E. B. Otto and C. E. Otto, *Ind. Eng. Chem., Anal. Ed.* **13,** 65 (1945).
[225] H. Fischer, *Z. anal. Chem.* **73,** 54 (1928).
[226] J Ackerman, *J. Phys. Chem.* **36,** 780 (1932).

with the strength of the dye adsorption. The fading of dyes is probably due to an oxidation that is speeded up by light.

Relatively few of the numerous dyestuffs possess a constitution suitable for the formation of lakes, *i.e.*, a content of inner complex-forming groups in the dye molecule. Hence it seems logical to inquire about the behavior of differently constituted dyes toward metal hydroxides. Consideration should be given first of all to the acid-base indicators. Because of dissociation and constitutional changes, their water or water-alcohol solutions undergo characteristic color changes at certain pH values. A pertinent example was discussed on page 501, where the behavior of alumina toward Congo red was described. This indicator is adsorbed initially with the blue color of the free Congo acid, and the transformation to the red color of the salts of Congo acid then follows gradually. Kolthoff[226a] described another striking instance of this kind. He found that alkali-free, washed lanthanum hydroxide is tinted in the basic pH range with the color of thymolphthalein, despite the fact that $La(OH)_3$ is far too insoluble to render water alkaline and thus cause the indicator to change color. Sachs[226b] has made very interesting studies of the action of freshly precipitated, well-washed hydroxides and basic salts toward a water or water-alcohol solution of phenolphthalein. He found that the hydroxides of Bi, Pb, Cu, Cd, Co, Ni, Zn, and Mg, and also the basic salts of Pb, Cu, Cd, Co, Ni, and Mn, are tinted, whereas the hydroxides of Sn, Sb, Al, Cr, and Fe remain unchanged. Accordingly, it is especially the basic hydroxides which are capable of being tinted by phenolphthalein, which has a weak acid character. However, there are exceptions, as exemplified by the hydroxides of Al, Cr, and Fe. The colorless oxides and basic salts are tinted with the red color of the quinoidal form of the phenolphthalein. Mixed colors result when the hydroxides or basic salts are themselves colored. Washing with water removes the coloration, which is restored by renewed spotting with phenolphthalein. Freshly precipitated products are tinted much more deeply than aged materials. The tinting of hydroxides and basic salts by indicators that are acidic in nature, is regarded as a result of surface reactions, in which, because of salt-like binding of the indicator anion, there is the same transformation into the quinoidal form of the indicator as results from the action of OH^- ions in solution.[226c] If an inner complex

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[226a] I. M. KOLTHOFF, *Kolloid-Z.* **68**, 169 (1934); *J. Phys. Chem.* **40**, 1027 (1936).

[226b] G. SACHS, *J. Am. Chem. Soc.* **62**, 3514 (1940).

[226c] W. M. DEHN, *J. Am. Chem. Soc.* **54**, 2947 (1932), obtained formula-pure colored metal compounds with phenolphthalein by starting with the metal hydroxides. On the basis of the analytical data, he assumes that addition compounds of metal

binding through activity of auxiliary valences is disregarded, the type of adsorption is, in principle, analogous to that involved in the production of lakes, namely, salt-like binding of the indicator on the surface of metal hydroxide particles without formation of salts in a special, separate phase. The tinting of precipitated metal hydroxides by dyestuff indicators is of analytical interest. The experiments of Sachs show that there undoubtedly is a certain selectivity in the behavior of basic metal hydroxide. In this connection it may be noted that intensive tinting of certain metal hydroxides can be accomplished if the latter are produced by precipitation with ammonia containing phenolphthalein. Red precipitates, which can be washed with hot water without noticeable fading, are given with $La(OH)_3$, $Th(OH)_4$, and $Ce(OH)_3$. In contrast, $Al(OH)_3$, $Be(OH)_2$, and $Zr(OH)_4$ are practically uncolored and even a single washing with water serves to remove all of the dye.[226d] Holler[226e] has pointed out that spotting with 1% alcoholic solution of phenolphthalein can be used to detect $Cd(OH)_2$ in the presence of ten times as much $Cu(OH)_2$, since the former is tinted crimson and the latter pastel blue.

In view of the many dyes that act as acid-base indicators, it seems entirely possible that some will be found which will exceed phenolphthalein in selectivity with respect to their adsorbability on metal hydroxides. Tests should also be made to discover whether tinted products have different resistances toward alkaline oxidants, with a view of applying such differences to analytical problems. The adsorption of indicator dyes must also be studied with respect to titrimetric procedures. If an alkali hydroxide is added to a metal salt solution in the presence of an indicator, a surface reaction of finely divided particles of the precipitate with the indicator may lead to a color change before the solution itself has become alkaline, i.e., before the true equivalent point has been passed. In his discussion of so-called colloidal errors, Kolthoff[226f] called attention to this source of error. He assumed that a surface reaction was the cause of the adsorption of the indicator when lanthanum hydroxide was tinted by thymolphthalein.

This discussion of the adsorptive taking-up of dyes by metal hydroxides will be concluded by citing an observation which points to an adsorption mechanism that differs from those previously considered.

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hydroxides with phenolphthalein are formed. The present writer believes that the colored products can be regarded as metal salts of phenolphthalein containing water of crystallization.

[226d] F. FEIGL, unpublished studies.

[226e] A. C. HOLLER, *J. Am. Chem. Soc.* **63**, 873 (1941).

[226f] I. M. KOLTHOFF, Acid-Base Indicators, New York, 1937, p. 354.

Eegriwe[220k] showed that the presence of Mg ions alters the behavior of an ammoniacal solution of *p*-aminophenol. Normally, when shaken in the air, this material slowly oxidizes and the solution turns light yellow, and eventually yellowish brown. Under the present conditions, a precipitate of $Mg(OH)_2$ is formed and it gradually turns blue. As little as 0.2γ of Mg can be detected in this way. It must be assumed that either an oxidation product of the aminophenol of quinoidal nature is adsorbed with a resulting change of color, or that an unstable blue intermediate product of the oxidation is stabilized because of the adsorptive binding. It is not known whether this type of adsorption can occur also with other metal hydroxides. In accordance with the foregoing discussion, the taking up of dyestuffs is regarded as chemical adsorption, in which, through stoichiometrically defined surface reactions, the dyestuff may be held by three different types of binding. Although certain types of binding are characteristic for the various types of dyestuffs, nevertheless, the same dyestuff may be taken up in different ways, depending on the nature of the adsorbent and the experimental conditions. For instance, diphenyl-carbazide and hydroxyanthraquinones, the typical lake-formers for metal oxides, can react in the manner of adsorption indicators with sparingly soluble crystalline metal salts. Possibly, many cases of tinting of $Mg(OH)_2$ and $Cd(OH)_2$ by dyestuffs, which heretofore have been regarded as lake formation, should rather be viewed as a binding of the adsorption indicator type.

In all the examples of the adsorption of dyestuffs considered in this section, the dyestuff was in true solution, and consequently could enter into surface reactions in molecularly or ionically dispersed form. There are dyestuffs, however, which are partly present in solution as colloids, and the colloidal portion may be in equilibrium with the truly dissolved portions. Certain dyestuffs are so-called colloidal electrolytes and form colloidal ions in solution. In such instances, the process of chemical adsorption on a solid can consist of an addition or exchange reaction of surface particles of the two phases. In this sense, it would be proper to speak of a solid-solid adsorption, in which the real adsorption layer would be the interfacial layer made up of the two contiguous surfaces. It would then depend primarily on the nature of the colloidal dyestuff, whether an adsorbate made up of the two solid phases is stable, or whether the unreacted part of the colloidal dyestuff breaks away, leaving a product that corresponds to an adsorbate from a molecular dyestuff solution. The experiments of Bayliss (p. 501) should certainly be considered from this viewpoint, and also certain dyestuff precipitations (to be mentioned later).

[220k] E. EEGRIWE, *Z. anal. Chem.* **118**, 98 (1939).

ADSORPTION COMPOUNDS

It has been repeatedly pointed out that the adsorption of dissolved materials on solids involves a binding between the adsorbed material and the adsorbent that together make up the adsorbate. Consequently, every adsorption on solids can be fundamentally regarded as producing an adsorption compound, no matter whether the active binding forces are of the type of principal or auxiliary valences or both jointly. However, the term "adsorption compound" is usually and properly reserved for adsorbates in which there is no great disproportion in the molar amounts of the adsorbed material and adsorbent, but where, instead, a rational relationship is approached.[227] In view of the great variety of kinds of adsorption, it is clear that it is not always possible to distinguish strictly between adsorption and the production of an adsorption compound. Intermediate systems are encountered and it is a matter of viewpoint as to whether they should be regarded as cases of adsorption or adsorption compounds. Instances are known where the prevailing conditions cause such marked variations in the extent of the adsorption that it is entirely proper to speak of the event as an adsorption sometimes, and as an adsorption compound production at others. However, it is not merely the lack of a sharply defined boundary between adsorption and adsorption compound that provides difficulties; attempts to differentiate adsorption compounds from stoichiometrically defined compounds (so-called Dalton compounds) also pose problems in some cases. Adsorption may be antecedent to the formation of a definite-chemical compound (see p. 502). Consequently, account must be taken of the possibility that the product of an adsorption, which, because of the molar ratio of the respective components can be regarded as an adsorption compound, does not necessarily have to be stable. There may be a gradual decomposition of this system into unaltered adsorbent and a stoichiometrically defined compound.

The components of adsorption compounds may be organic, inorganic, or mixed. Accordingly, purely organic and purely inorganic, as well as mixed organic-inorganic adsorption compounds, are known. In addition to this classification that is based on the nature of the components, it is also possible to classify adsorption compounds according to the degree of dispersion of the components which are uniting to form these compounds. Thus, adsorption compounds are known which have resulted from the action of molecularly or ionically dispersed materials on a solid that is in the colloidal range (gel or sol). This type of adsorption compound comes

[227] Sometimes the term adsorption compound (adsorption complex) is also used for every type of adsorption, regardless of its extent.

closest to adsorption in the most usual sense of the term. Another kind of adsorption compound arises from the union of two components which are both in the colloidal range of dispersion. Fundamentally, this corresponds to solid-solid adsorption. Hence, it is common to all adsorption compounds that at least one participant in their production is in the colloidal range. Since adsorption compounds are the product of surface reactions of gel or sol particles they are always amorphous. A further general characteristic is that the composition of adsorption compounds depends markedly on the conditions (temperature, concentration, *etc.*) that obtain during the formation of the compound. In many instances, the molar ratio provides a criterion for determining which of the components of the adsorption compound is the adsorbed material and which the adsorbent. This distinction is more difficult when Dalton compounds are closely approximated, and it can lose all real significance when colloidal particles unite to form adsorption compounds. All types of adsorption compounds can have analytical importance insofar as their formation is accompanied by quantitatively selective precipitations or characteristic color effects.

Purely inorganic adsorption compounds are met in hydroxide precipitations of metal ions, and also when acids bring down water-insoluble solid acid anhydrides from solutions of alkali salts of weak acids (SiO_2, WO_3, *etc.*). Such products often contain too much water to permit their total water content to be included when calculating the formulas of these materials as hydrates of oxides or as hydroxides. The excess water, so far as it is not mechanically enclosed in cavities of gelatinous products, is bound adsorptively for the most part. The quantity of such adsorbed water, which determines the intensity of shade of colored oxides, depends on the precipitation conditions through which, quite generally, the surface of newly formed phases is influenced. It is characteristic of water which is adsorptively bound to an oxide, that, on heating under constant pressure, *i.e.*, at constant partial pressure of the water vapor, the water is given off continuously. This is in contrast to the behavior of water of crystallization or hydration, which is released in distinct stages to produce less hydrated or anhydrous compounds. This stepwise loss of water signifies that a compound which carries water of crystallization or hydration remains unchanged in composition through a certain temperature interval, and only when a certain higher temperature is reached does it give up water and continue to do so until the formation of a less hydrated or water-free compound is accomplished.[228]

[228] Quite analogous to these dehydration curves at constant pressure (isobars) are the dehydration curves at constant temperature and decreasing pressure (isotherms). Here again the dehydration curves produced by adsorbed water are continuous and those for water of crystallization or hydration are stepped, respectively.

Frequently, adsorption compounds of water with acidic or basic oxides are, in gel or sol form, the starting materials for the production of adsorption compounds with substances in true or colloidal solution. A well known example, discovered by Bunsen, is the fixing of arsenious acid on freshly prepared hydrous ferric oxide (see p. 511). This material takes up so much As_2O_3 that it is proper to speak of the production of an adsorption compound. With aged ferric oxide, the quantity of arsenious oxide, which is taken up in accord with an adsorption isotherm, falls off decidedly and, if dried ferric oxide is used, the values drop to practically nothing. Consequently, this system runs a gamut from adsorption of minute amounts and includes an adsorption compound. At the same time it also demonstrates, as might have been expected, that the production of adsorption compounds is likewise related to the extent of the specific surface. Obviously, there exist limiting values of the specific surface both for the occurrence of an adsorption as well as for the formation of adsorption compounds.

The earliest example of the use in analysis of the production of an adsorption compound with participation of an ionically dispersed material as adsorbed material is due to Reynoso.[229] He found that phosphoric acid is coprecipitated by stannic acid. This retention occurs if metallic tin is treated with concentrated nitric acid in the presence of phosphate. The resulting metastannic acid functions as the adsorbent and the total phosphate content of the solution will be taken up if the tin is present in sufficient amount and provided that hydrochloric acid is absent. When stannic acid is formed in a solution that contains phosphate and hence acts in *statu nascendi*, about 6–13 mols of stannic acid per mol of phosphoric acid are required to accomplish the complete removal of the phosphate ions. Mecklenburg[230] showed that previously prepared stannic acid gel (containing about 10% SnO_2) can also be used to remove phosphoric acid. In this case, the molar ratio is about 1:40, corresponding to the lesser surface of the stannic acid gel. He[231] subsequently showed that the taking up of phosphoric acid by metastannic acid is a typical adsorption process, since the quantity of phosphoric acid fixed depends on the phosphate concentration of the solution, on the age of the stannic acid, and on the manner in which the adsorbent was prepared. The adsorption of phosphoric acid by metastannic acid is used in qualitative analysis. It is applied before carrying out the ammonium sulfide precipitation, the object of which is to separate the ions (Fe, Co, Ni, *etc.*) precipitable by S^{--} ions, from the ions of the alkali earth and alkali metals (Ba, Ca, Mg, *etc.*). This separation is not feasible when phosphate ions

[229] A. REYNOSO, *J. prakt. Chem.* **54**, 267 (1851).
[230] W. MECKLENBURG, *Z. anal. Chem.* **52**, 293 (1913).
[231] W. MECKLENBURG, *Z. anorg. allgem. Chem.* **74**, 215 (1913).

are present because the members of the $(NH_4)_2CO_3$ group precipitate as phosphates in neutral or basic solution. When the P_2O_5-adsorption procedure is employed it must be remembered that tri- and quadrivalent metals (especially Fe, Cr, Ti) are also adsorbed to a considerable degree by stannic acid. Consequently, this method can be used only for qualitative purposes but not in quantitative work. The non-specificity of the adsorptive action of stannic acid is further shown by the fact that it can adsorb considerable quantities of antimonic acid. Experience gained in the analysis of tin and antimony alloys (especially bronzes) has taught that treatment of such materials with concentrated nitric acid invariably produces stannic acid which is contaminated with antimony. Bertiaux[232] showed that the retention of antimony is quantitative if the Sn:Sb ratio exceeds 1:5. Hence, the addition of tin will bring about the quantitative deposition of the antimony when antimony-richer alloys are treated with nitric acid. In all likelihood, the antimony is held by the stannic acid in the same manner as phosphoric acid is bound by this absorbent.

The adsorption of phosphoric acid on stannic acid gel is probably connected with the possibility of a principal valence linkage between the tin and the phosphate radical. Although no formula-pure stannic phosphate has been isolated as yet, nevertheless, Gattermann and Schindhelm[233] found that the addition of freshly prepared stannic chloride solution to weakly acidified phosphate solutions produced, even at room temperature, a precipitate that, in contrast to stannic acid, filters well. Furthermore, the complete precipitation of the phosphoric acid requires not more than about 1.5 times as much stannic chloride as would be necessary to form $Sn_3(PO_4)_4$. Accordingly, in this Gattermann procedure, which has been recommended for the removal of phosphoric acid,[234] the formation of stoichiometric tin phosphate or basic stannic phosphate has been very closely approached. This finding makes it probable that the tin atoms on the surface of the SnO_2-gel particles are in direct combination with phosphate radicals when phosphoric acid is irreversibly adsorbed on stannic acid gel. This could be the case without the production of a new $Sn_3(PO_4)_4$ phase if the binding of SnO_2 molecules in the SnO_2 gel through O-atoms is not ruptured completely. In a formal sense, this postulate is equivalent to the production of a basic stannic phosphate on the SnO_2 surface.

Adsorption compounds can be formed by basic or acidic oxides in either their gel or sol forms. The latter are involved when colloidally

[232] L. Bertiaux, *Bull. soc. chim.* **1946**, 102.
[233] L. Gattermann and H. Schindhelm, *Ber.* **49**, 2416 (1916).
[234] Compare, however, N. Tarugi, *Boll. chim. farm.* **61**, 545 (1922).

dispersed hydrolysis products of metal salts react with materials in true or colloidal solution and form precipitates. Under such circumstances, the reaction appears to occur in solution, but in reality particles of colloidal size enter into reaction. They are derived from the hydrolysis equilibrium and so are replaced as soon as they are consumed. Since they enter into reaction on their surfaces, the extent of their surface development, and the particular nature of the reactants, determine whether there is a complete or only a partial reaction of the colloidal particles. Obviously, Dalton compounds can result only when there is complete reaction. In the other case, there will always be deviations from a stoichiometrically defined composition, and the divergences will be more serious the less extensive the reactive surface. A reaction that was first studied by Loewenthal,[235] and later by others,[236] shows this effect quite plainly. If stannic chloride solutions are added to a given constant volume of a solution of potassium ferrocyanide, yellow precipitates are obtained. The composition of the solid product, i.e., the ratio $Sn:Fe(CN)_6$ varies with the time that has elapsed since the $SnCl_4$ solution was prepared. Table XXV gives some of the findings:

TABLE XXV

Age of $SnCl_4$ solution, days	Amount of $SnCl_4$ solution to precipitate 0.5 g. $K_4Fe(CN)_6$, cc.	Composition of precipitate. Ratio $\dfrac{Sn}{Fe(CN)_6}$
0	6	1.5
7	10	2.3
14	14	3.3
89	27	6.5
126	32	7.5
162	36	8.5

In view of these findings, it is evident that the reaction between $SnCl_4$ and $K_4Fe(CN)_6$ is not ionic, and hence does not involve Sn^{++++} ions directly. Otherwise there would be no reason why freshly made solutions should not act the same as aged solutions. Even assuming that the hydrolysis equilibrium shifts, in the course of time, toward the side of the hydrolysis products, there could be no decided difference in the concentration of Sn^{++++} ions. Consequently, it is necessary to assume that the $K_4Fe(CN)_6$ reacts with the hydrolysis products of the stannic chloride, i.e., with colloidally dispersed $Sn(OH)_4$ particles. The colloidally

[235] L. LOEWENTHAL, J. prakt. Chem. **77**, 321 (1859).

[236] R. LORENZ, Z. anorg. Chem. **9**, 369 (1895); W. MECKLENBURG, ibid. **64**, 372 (1909); C. F. BARFOED, J. prakt. Chem. **101**, 368 (1867).

dispersed hydrolysis products doubtless have a greater surface in fresh stannic chloride solutions than in older ones, in which the particles have agglomerated, although this condition is not directly visible. The result is that a given quantity of $K_4Fe(CN)_6$ requires less of a freshly prepared stannic chloride solution for complete precipitation than of an aged solution of the same concentration. In neither case is the precipitate pure $SnFe(CN)_6$ but is an adsorption compound of variable composition.

This instance of the dependence of the composition of an adsorption compound on the surface condition of the colloidally dispersed reactants can also be considered from the standpoint of the reactivity of the colloid particles. It might be said that aged particles, because of their diminished surface, are less reactive than younger particles. It may be expected that such a surface influence will make itself evident quite generally in reactions involving colloidal particles, and hence also in those that give rise to soluble products. Actually, Bourion and Senechal[237] found that solutions of hydrous chromic oxide in alkali, which contain colloidally dispersed particles of $Cr_2O_3 \cdot aq$ peptized by alkali, do not always form chromate to the same extent on treatment with hydrogen perioxide. This oxidation proceeds to a greater extent in freshly prepared dispersions than in older ones. The decreased activity on standing is due to a gradual change in particle size, a change that is sufficiently marked with a concentrated sol to result in partial precipitation in a short time.

The inorganic adsorption compounds discussed in the foregoing paragraphs were produced by reactions on the surface of particles in the colloidal range, without the formation of a new phase. The reactions involved were of the double decomposition type. Obviously, adsorption compounds can also result from addition reactions. A model example is the so-called Schlagdenhauffen reaction.[238] In this, freshly precipitated and washed magnesium hydroxide is tinted red-brown by a potassium iodide-iodine solution. The coloring effect is due to an adsorption of iodine on $Mg(OH)_2$, which accordingly is able to withdraw and bind to itself the molecular iodine that is coordinated in the polyiodide ion $(I \cdot I_2)^-$. Even though the binding to the hydroxide is not very firm, it still permits the colored product to be washed with water without significant change. Treatment with solutions of NaOH, Na_2SO_3, $Na_2S_2O_3$, or concentrated solutions of KI, as well as organic liquids that dissolve free iodine, will remove the iodine from the adsorption compound, and colorless $Mg(OH)_2$ is left. The best conditions for forming the brown product are: (a) to treat a magnesium salt solution that contains KI_3 with

[237] F. Bourion and A. Senechal, *Compt. rend.* **168**, 59, 89 (1919).
[238] F. Schlagdenhauffen, *Z. österr. Apoth. Ver.* **16**, 348 (1878).

an alkali, or (b) to add to a neutral magnesium solution an iodine solution that has just been decolorized by means of alkali, i.e., with a freshly made solution of alkali hypoiodite.[239] The following equilibrium exists in hypoiodite solutions:

$$I_2 + 2OH^- \rightleftharpoons I^- + OI^- + H_2O$$
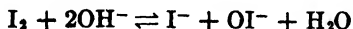
When this equilibrium solution is brought together with a solution of a magnesium salt, the production of $Mg(OH)_2$ not only removes OH^- ions, that are replenished at once by the reestablishment of the equilibrium, but simultaneously equivalent quantities of iodine are set free. Consequently, the most ideal conditions are provided for an adsorption of iodine on $Mg(OH)_2$ in *statu nascendi* and in the colloidal range. If a freshly prepared solution of hypoiodite is employed, or if alkali is added to an iodine-containing magnesium solution, there will still be a clearly visible production of the colored adsorption compound from solutions that are too dilute to produce a visible precipitate of $Mg(OH)_2$. The sensitivity (identification and concentration limit) of the reaction that leads to the production of the adsorption compound is far beyond that of the reaction which results in the formation of the $Mg(OH)_2$, which functions here as adsorbent. It need not be stressed that very considerable analytical value exists in such an enhancement of the sensitivity of a precipitation reaction, entirely apart from the frequent selectivity of the adsorption. In the present instance, the selectivity shows itself in the fact that other metal hydroxides either do not form brown adsorption compounds with iodine or do so to a much lower extent (e.g., hydroxides of rare earths). Accordingly, the Schlagdenhauffen reaction is an excellent test for magnesium. It is possible to determine small amounts of magnesium colorimetrically by comparing hydrosols of the adsorption compound.[240]

A very interesting counterpart to the adsorption of iodine on magnesium hydroxide is the taking up of iodine by basic lanthanum acetate. This action was first reported by Damour.[241] The adsorbent is prepared by treating lanthanum acetate solution with ammonia; when spotted with iodine the freshly precipitated material is turned deep blue. Biltz[242] proved that no definite compound is formed in this color reaction; the iodine is taken up by an adsorption process, which occurs with both

[239] A. Hamy, Compt. rend. **183**, 129 (1926); W. J. Petraschenj, Z. anal. Chem. **71**, 291 (1927).

[240] Compare P. Denigès, Compt. rend. **175**, 1207 (1922); A. K. Babko, Chem. Abstracts **29**, 7859 (1935).

[241] A. Damour, Compt. rend. **43**, 976 (1857).

[242] W. Biltz, Ber. **37**, 719 (1904).

hydrogels and hydrosols of basic lanthanum acetate.   The action involves an adsorption compound between basic acetate and iodine, that is quite similar to the product obtained with iodine and starch.   As in the latter instance, rather stable blue colloidal solutions can be prepared, and the sensitivities of the iodine-starch and the iodine-lanthanum reactions are of about the same order of excellence with regard to the detection of iodine.   Krüger and Tschirch[243] investigated the lanthanum-iodine reaction thoroughly.   Their findings indicate that it represents a highly specific adsorption since only basic acetate but not the hydroxide of lanthanum or basic acetates of other rare earths show this color reaction. Unfortunately, the reaction has slight sensitivity as a test for lanthanum (2–3 mg./l.) and this value is lessened decidedly when relatively small amounts of other rare earths are present.   On the other hand, Krüger and Tschirch found that the iodine-lanthanum reaction can be used as a quite sensitive and selective test for acetate (0.1 mg. acetic acid/l.). Propionic acid behaves like acetic acid, but substituted acetic acids are inactive.

A fundamentally important method of producing adsorption compounds is visibly illustrated by the Schlagdenhauffen reaction carried out with alkali hypoiodite.   The reaction of magnesium solutions with alkali hypoiodite produces magnesium hydroxide and also free iodine, which is only slightly soluble in water.   The iodine is fixed on the magnesium hydroxide, i.e., instead of two separate solid phases—$Mg(OH)_2$ and I_2—a homogeneous, brown product results, which, because of the necessary equivalent production of these materials, comes close to being a true Dalton compound with respect to composition.   However, the products formed by means of hypoiodite must likewise be regarded as adsorption compounds because products of the same kind can be obtained with variable excesses of $Mg(OH)_2$ (through action of iodine on previously precipitated $Mg(OH)_2$, or by adding alkali to an iodine-containing magnesium solution).   Other reactions that can be formulated stoichiometrically are known in which two water-insoluble products are formed in equivalent amounts either simultaneously or in immeasurably rapid succession.   In such cases it may well be assumed that adsorption will occur if, through the action of surface residual valence forces, there is any tendency at all toward adsorption.   Both of the insoluble products have their maximum surface exposure in *statu nascendi*, and hence the optimum conditions are provided in any case for a mutual adsorption of particles in the colloidal range.

An interesting example of the simultaneous formation and adsorption

[243] D. Krüger and E. Tschirch, *Ber.* **62**, 2766 (1929); **63**, 826 (1930); *Mikrochem.* **8**, 218 (1930).

of two insoluble reaction products in the course of a reaction is provided by the action of ammoniacal silver solution on cerous solutions. The reaction:

$$Ce^{+++} + [Ag(NH_3)_2]^+ + 4OH^- \rightarrow Ag° + \overset{.}{Ce}(OH)_4 + 2NH_3$$
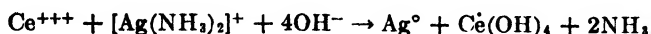
produces a deep black precipitate and not the mixed color of the products even when an excess of cerium is present. Biltz and Zimmermann,[244] who studied this reaction, assume that an adsorption compound is formed between the two insoluble reaction products. Analogous redox reactions occur if the Ce^{+++} ions are replaced by Fe^{++} or Mn^{++} ions, or if noble metal ions are used instead of Ag^+ ions, or the ammonia may have its place taken by any donor of OH^- ions. Black precipitates result in all these cases and they can be regarded as adsorption compounds between noble metal and higher oxides of non-noble metals.[245] The redox reaction between Ce^{+++} and Ag^+ ions can be applied as an unequivocal test for cerium in the presence of all rare earths. The adsorption compound between $Mn(OH)_4$ and silver has special analytical value. It is the basis of sensitive tests for silver[246] and ammonia,[247] and also of convenient tests for free basic oxides in glass, ash, and similar materials.[248] Furthermore, it is possible to distinguish between calcite and aragonite by spotting the specimen with a neutral $AgNO_3$-$MnSO_4$ solution; aragonite is more alkaline and, accordingly, it initiates the redox reaction between Ag^+ and Mn^{++} ions more quickly than the less basic calcite.[249]

A well known reaction, in which two reaction products combine in the colloidal state to produce an adsorption compound, is the formation of purple of Cassius (see p. 470). In this case, the primary reaction: $2Au^{+++} + 3Sn^{++} \rightarrow 2Au° + 3Sn^{++++}$ (probably with intermediate pro-

[244] W. Biltz and F. Zimmermann, *Ber.* **40**, 4982 (1907).

[245] The experience of the writer indicates that the composition of the precipitate obtained by adding ammonia to a solution containing Mn^{++} and Ag^+ ions does not correspond to the reaction: $Mn^{++} + 2Ag^+ + 4OH^- \rightarrow Mn(OH)_4 + 2Ag°$, but contains far less silver. Probably, the reaction, which results in an adsorption compound between silver and higher manganese oxides, can be resolved into partial reactions, such as (a) $Mn^{++} + 2OH^- \rightarrow Mn(OH)_2$ and (b) $Mn(OH)_2 + Ag^+ + OH^- \rightarrow Mn(OH)_3 + Ag°$. This would mean that at first $Mn(OH)_2$ particles form, and they can undergo with Ag^+ ions a surface redox reaction, in which the resulting free silver remains in adsorptive binding with unchanged oxide. This conception, which can also apply to the analogous redox reactions cited previously, is strengthened by the fact that precipitated and washed $Ce(OH)_3$ and $Mn(OH)_2$ immediately give a black coloration on treatment with ammoniacal silver solution.

[246] N. A. Tananaeff and J. T. Tananaeff, *Z. anal. Chem.* **106**, 167 (1936).

[247] F. Feigl, *Mikrochemie* **13**, 134 (1933).

[248] Y. Kondo, *Mikrochim. Acta* **1**, 154 (1937).

[249] F. Feigl and H. Leitmeier, *Mineralog. u. petrog. Mitt.* **45**, 447 (1934).

duction of univalent gold) is followed almost immediately by hydrolysis of the resulting Sn^{++++} ions: $Sn^{++++} + 4H_2O \rightleftharpoons Sn(OH)_4 + 4H^+$. If the reaction is carried out in concentrated solution, the adsorption compound between gold and $Sn(OH)_4$ appears as a red-brown precipitate, whereas in dilute solution the adsorption compound remains in colloidal dispersion as a purple-red hydrosol in which the $Sn(OH)_4$ acts as a protective colloid for the colloidal gold particles.

In the foregoing redox reactions, adsorption compounds result from a mutual adsorption of insoluble reaction products, formed concurrently or in immeasurably rapid succession, and acting either in colloidal dispersion or in the colloid range. It seems logical to suppose that, when two ionic species undergo precipitation with the same precipitant, either simultaneously or in very rapid succession, the particles of the precipitates in the colloidal range of the sol or gel form may combine to form adsorption compounds if there is any tendency for this to occur. A partner in an adsorption compound formed in this manner may possibly have a solubility and a reactivity different from that which it possesses when it exists as a separate independent phase. The writer believes that this difference may be one reason for the anomalies in the chemical behavior of oxides and sulfides that are precipitated together, and which were discussed in Chapter V. The fact that such anomalies of coprecipitated products are not entirely general and do not occur to equal extents, but rather are selective and dependent on the precipitation conditions, is in agreement with the assumption that adsorption compounds are formed in these instances.

The entrance of hydrous basic and acidic metal oxides into mixed inorganic-organic adsorption compounds is of great analytical import. Instances of such adsorption compounds have already been encountered in the discussion of the adsorption of dyes, and particularly in the so-called color lakes. The latter, or more precisely, the metal color lakes were defined as adsorption compounds in which the organic dye component is capable of being bound at the same time by both principal and auxiliary valences (inner complex binding) to the metal atom of the oxide. As a logical extension of this concept, colored adsorption compounds of metal oxides with colorless acidic organic compounds that are capable of forming inner complex compounds can likewise be included among the color lakes. Side by side with the metal color lakes for which the inner complex binding of the organic component is characteristic, there can be placed the union of true or colloidally dissolved dyes with metal oxides effected solely by auxiliary valences. In this connection, it must be remembered that water solutions of salts of polyatomic dyes of weak basic or acidic character contain colloidally

dispersed hydrolysis products, and also that many dyes are colloidal electrolytes, *i.e.*, in solution they are partly present as colloid ions. Such colloid particles of dyes can be irreversibly adsorbed on oxide particles in the colloidal range, and, if there is no extreme disproportion in the molar ratio of the adsorbed material and adsorbent, such products may also be regarded as adsorption compounds.

The precipitates obtained by treating solutions of an alkali tungstate with mineral acid solutions of benzidine (compare Chapter VI) and other polyatomic organic bases are inorganic-organic adsorption compounds. Formula-pure tungstates of these bases are never precipitated under such circumstances; the precipitates contain much more tungsten than corresponds to a definite salt. The composition depends on the precipitation conditions, and especially on the tungstate concentration. The deviation from the composition of a definite salt is due to the fact that acidification of alkali tungstate results to only a slight extent in molecular or ionogenically dissolved tungstic acid, which can combine to form a Dalton compound with the hydrochloride of an organic base (B):

$$2B \cdot HCl + H_2WO_4 \rightarrow (2B) \cdot H_2WO_4 + 2HCl$$
$$2BH^+ + WO_4^{--} \rightarrow (2B) \cdot H_2WO_4$$
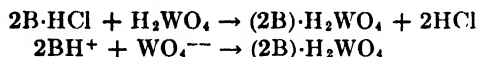
For the most part, acidification of alkali tungstates produces $WO_3 \cdot aq$, which, depending on the concentration of the tungstate solution, either separates as a gelatinous precipitate or stays in colloidal solution. The hydrochloride of an organic base can only react on the surface of particles of tungstic acid in the colloidal range of the hydrosol or hydrogel form; the reaction cannot extend completely through the particles to form a definite tungstate. Considerable analytical importance attaches to the fact that, because of the production of adsorption compounds between tungstic acid and organic bases, the colloidal dispersion of the tungstic acid is broken up. Consequently, dilute alkali tungstate solutions, which remain clear on the addition of mineral acids and give no visible precipitate of $WO_3 \cdot aq$, can immediately produce a distinct precipitate in the presence of organic bases of high molecular weight. This effect is used for the qualitative detection, and particularly for the quantitative determination, of tungsten, as the adsorption compounds formed are readily ignited to WO_3.

The so-called tannin precipitations are representatives of the very interesting class of inorganic-organic adsorption compounds during the formation of which the organic component is in the colloidal range. Tannin is a collective name that is applied to water-soluble mixtures of ester-like compounds of various sugars with phenolcarboxylic acids. These mixtures are found in many plants. Pentadigalloyl glucose (I)

has been prepared synthetically;[250] its properties are strikingly similar to those of natural Chinese tannin.

(I)
Pentadigalloyl glucose

(II)
m-digallic acid (didepside of gallic acid)
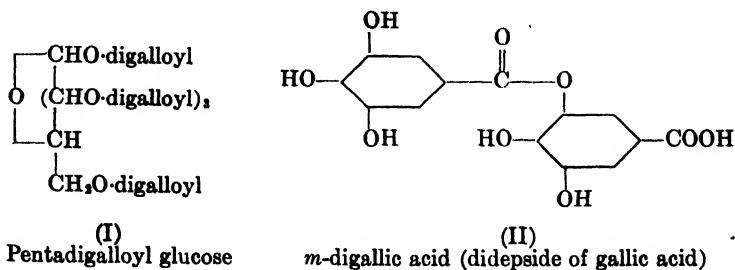
Tannins are polyatomic compounds; their excellent water-solubility is doubtless due to their high content of phenolic OH groups which act as hydration centers. However, the water solutions are not true but colloidal solutions, or are quite close to colloidal dispersions because of the high molecular weights and large molecular volumes of the tannins. Probably these solutions also contain polymers of the tannins. If water solutions of tannins are treated with solutions of hydrolyzable metal salts, that contain positively charged colloidal particles of basic hydrolysis products (oxyhydrates), flocculent precipitates are formed.[251] The precipitate is often regarded as the result of a mutual discharge and flocculation of the colloidal particles with no consideration of the underlying chemical processes.[252] The latter may consist of the elimination of water through condensation of basic OH groups on the surface of the oxyhydrate particles with the phenolic OH groups of the tannin particles. The resulting adsorption compound between oxide and tannin particles is less soluble than the respective oxide and tannin particles by themselves. Consequently, there is a constant disturbance of the hydrolysis equilibrium of the particular metal salt and therefore a quantitative precipitation of the metal, provided the pH is not too low. Solutions of hydrolyzable metal salts that are so dilute that no visible precipitate forms on the addition of ammonia, can give definite precipitates with tannin, aided if necessary by the addition of alkali acetate or ammonia. Size and weighting effects are probably responsible for the fact that the precipitation of the tannin-adsorption compound is more sensitive than

[250] E. FISCHER and M. BERGMANN, *Ber.* **51**, 1760 (1918); P. KARRER, *Helv. Chim. Acta* **6**, 3 (1923).

[251] The term "adsorption" precipitant is used by J. F. FLAGG ("Organic Reagents, p. 30, New York, 1948), for tannin and other organic reagents which produce adsorption compounds.

[252] Compare W. R. SCHOELLER and A. R. POWELL, The Analysis of Minerals and Ores of the Rarer Elements, 2nd ed., p. 6. London, 1940.

the hydroxide precipitation of the metal which makes up the inorganic portion of the adsorption compound. Analogous effects are encountered with other adsorption compounds.

The foregoing reaction course, involving colloidal particles, can hold for tannin precipitations from weakly acid or buffered metal salt solutions. It has now been found, however, that tannin precipitations can occur also from ammoniacal metal salt solutions that are masked by means of tartrate, citrate, oxalate, sulfosalicylate, *etc.* Furthermore, tannin precipitations can be formed in ammoniacal copper solutions or ammoniacal solutions of ferrous dipyridyl and in uranyl solutions that contain ammonium carbonate. The respective metals are present in such solutions as complex ions, and the concentration of free metal ions is determined by the particular complex equilibrium, or the instability constant of the complex. The metal ion concentration is doubtless extremely low in the presence of strong complex-formers that prevent the precipitation of the hydroxide. Therefore, it is quite questionable whether colloidal particles of metal hydroxides are present in such masked solutions. Even though this is the case, alkaline solutions probably contain negatively charged particles, which accordingly react with negatively charged particles of tannin (perhaps of its oxidation products). This could only be possible in the form of a surface reaction of the particles as outlined previously. It is much more likely that precipitation reactions of masked ammoniacal metal salt solutions with tannin are due to the reaction of tannin particles with metal ions that come from the complex equilibrium. The formula (I) representing a tannin with acidic phenol components shown in (II) indicates that the tannin surface is so thickly populated with phenolic OH groups that a metal-phenolate binding can occur without forming a definite tannate as a separate phase. The concept of a direct reciprocal action between phenolic OH groups and metal ions is also supported by the fact that solutions of gallic and digallic acid, which are true solutions, likewise exhibit a precipitating action which is analogous to that of tannin, though often of lesser sensitivity. The writer believes that it is entirely possible that in acid and buffered solutions also, in which, along with hydrolysis products, there are goodly numbers of metal ions, it is the latter rather than the positively charged particles of the hydrolysis products which react with the negatively charged tannin particles. In addition, the possibility is not excluded that both methods of forming adsorption compounds of tannin proceed concurrently, and to extents that depend on the particular precipitation conditions. It is remarkable that not only hydrolyzing metal salts but also metal acids, such as vanadic and tungstic acid, produce precipitates with tannin. For such precipitates it cannot be

assumed that colloidal particles of the anhydrides of the metal acids and of the tannin are coagulated and precipitated through a compensation of charges, since both particles are charged negatively. Probably, here again, there are reactions between surface portions of the particles. It is conceivable that there is an ester-like binding of the tungstic or vanadic acid to the tannin to form a phenol ester. There is also a possibility that first of all a redox reaction takes place between W^{VI} or V^V and the oxidizable tannin with formation of lower, more strongly basic oxides, which then react with the tannin in the same manner as metal salts.

A discussion of the adsorption compounds of the colorless tannin must include the fact that numerous tannin precipitates are colored. For instance, the titanium precipitate is red, that of tantalum yellow, of niobium red-orange, of chromium greenish, of copper dirty brown, of vanadium blue-black, of tungsten brown, and of iron purplish-black. Some of these color reactions are extremely sensitive. Thus, the vanadium-tannin reaction appears to be one of the most sensitive vanadium reactions known. The iron reaction is so sensitive that it can be employed for the identification of tannins.[253] The color probably is connected with the fact that the reactive components in the tannins are always polyphenols with *ortho*-situated OH groups. When such a group is salified, a coordination of the metal atom to an oxygen atom of an adjacent OH group is possible and this corresponds to an inner complex binding. Accordingly, it appears proper to include the colored tannin adsorption compounds among the metal color lakes. Of course, the colored tannin adsorption compounds do not conform to the rule stated in connection with the metal color lakes, namely, that lakes form in the existence range of their underlying metal oxides. As was mentioned, quantitative precipitations of the tannin complexes are obtained in weakly acid, buffered, neutral, and even in masked ammoniacal solutions. This would seem to indicate that metal oxides are not present as the inorganic components of tannin-adsorption compounds, but that the latter result rather from surface reactions of the phenol groups of tannin with metal ions. However, there are valid reasons for believing that true metal color lakes are also formed beyond the precipitation range of the underlying metal oxides. An excellent example of this is given by the behavior of zirconium toward alizarin and other polyhydroxy-anthraquinones. The violet zirconium-alizarin lake can be obtained in the same manner as the other alizarin lakes, *i.e.*, by adding an alkaline solution to a zirconium solution. However, de Boer[254] found that

[253] Compare M. NIERENSTEIN, Section on Tannins, Allen's Commercial Organic Analysis, Vol. V. Philadelphia, 1927.

[254] H. J. DE BOER, *Chem. Weekblad.* **21**, 404 (1924).

alizarin reacts also with zirconium solutions containing hydrochloric acid and, according to the concentration, the product is either a violet precipitate or a violet coloration (hydrosol). In this case, there obviously is a constant disturbance of the hydrolysis equilibrium because of the removal of the colloidal hydrolysis product to form an alizarin lake, and this can lead to the quantitative precipitation of the zirconium. This exceptional behavior of zirconium with respect to lake-formation is the basis of specificity of the zirconium-alizarin reaction in acid solution, which has been employed extensively for analytical purposes. It is possible that the extraordinary behavior of zirconium is due to its marked tendency to form water-insoluble, acid-stable normal and inner complex salts (compare Chapter VI).

The foregoing discussion has dealt with the peculiarities of tannin precipitations. It was assumed that tannin precipitations result not only from reactions between colloidal particles, but also through surface reactions of tannin particles with metal ions, the latter case is one in which colloidal tannin should be regarded as the adsorbent and the metal ions as the material being adsorbed. The credit for recognizing the great analytical importance of tannin precipitations, particularly for gravimetric purposes, belongs to Schoeller and his school. In very interesting experimental studies, he and his coworkers (and later others) combined the tannin precipitations with masking effects and with maintenance of definite conditions of acidity. It thus became possible to develop important new methods for the separation and determination of rare and ordinary metals. Among others, it became possible, through fractional tannin precipitations, to accomplish the extremely difficult separation of tantalum from niobium with an accuracy never before attained. A more detailed discussion of the analytical utilization of tannin precipitations is beyond the scope of this text.[255]

Another instance of an inorganic-organic adsorption compound, in which an organic compound functions as adsorbent for an inorganic component that was previously in true solution, is the starch-iodine reaction. There is an extensive literature on this reaction, whose analytical importance needs no special emphasis.[256] Starch, a polysaccharide with the empirical formula $(C_6H_{11}O_5)x$, is contained in the cells of many higher plants. At room temperature it is water-insoluble, but on hydrolysis it is converted to monomolecular soluble glucose, $C_6H_{12}O_6$. According to the current views of starch chemistry, which has been the subject of an enormous number of pure organic and colloid

[255] See W. R. SCHOELLER and A. R. POWELL, op. cit.

[256] I. M. KOLTHOFF, Volumetric Analysis, Vol. II, p. 278. New York, 1947 see also the literature cited in (257).

chemical studies,[257] the polymerization consists of the glucosidic union of glucose residues or radicals (I), thus producing giant molecules with polymembered chains. These chains may be straight or branched. In starch it is possible to distinguish two constituents from each other, on the basis of the type and length of the chains that make up their molecules. These constituents are amylose and amylopectin. The amylose consists essentially of a polymeric homologous mixture of unbranched chains in which 100–700 glucose residues are united in a 1:4 glucosidic arrangement as shown in (II). Amylopectin consists of branched molecules of from 500 to more than 2000 glucose residues in which branching occurs on the average at every 25th glucose unit as shown in (III).

$$CH_2OH$$

schematically
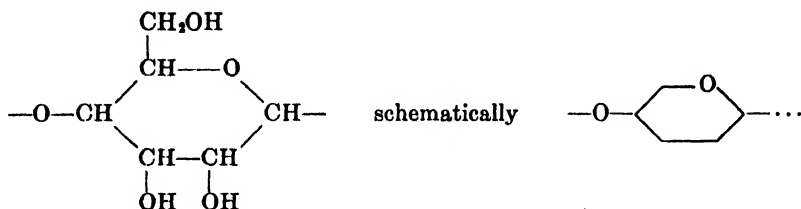
I. Glucose residue (unit)
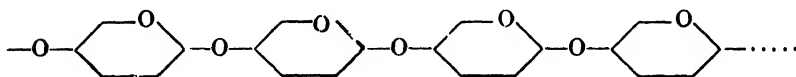
II Section of amylose chains

$$CH_2$$
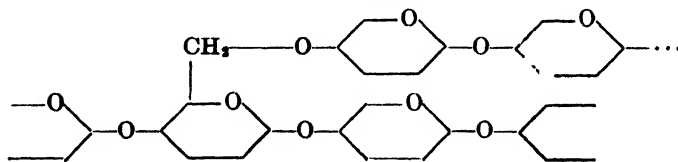
III. Branch point of amylopectin chains

In solid starch the giant molecules of amylose and amylopectin are joined, either to their own or the other kind, by auxiliary valences. A more or less extensive loosening of the auxiliary binding and hydration occurs in hot water. The hydrated amylose goes into solution and it should be noted that the amylose molecule is of colloidal dimensions in the lengthwise direction of the chain. The colloidal character is much more marked in the case of the hydrated amylopectin molecules because

[257] Comprehensive reviews are given in: K. H. MEYER, "Recent Developments in Starch Chemistry," in Colloid Science (edited by E. O. Kraemer), Vol. I, pp. 143–182. New York, 1942. M. SAMEC, "A Summary of the Chemistry of Starches," in Colloid Chemistry (edited by J. Alexander), Vol. IV, pp. 167–186. New York, 1932.

of the far greater number of glucose units in its branched chains. The hydrated giant molecules of amylose and amylopectin show a tendency to reunite into molecular aggregates. Since the high molecular weight colloid amylopectin constitutes about 85–95% of the starch, a swelling with not too much water results in the production of a paste (starch paste).

Amylose and amylopectin differ with respect to their behavior toward iodine. Only the former produces the familiar pure blue color in the iodine-starch reaction, whereas the product of the action of iodine on the branched amylopectin has a tinge of violet. Chain molecules with still more branches give a red color with iodine. Freshly prepared starch paste contains both amylose and amylopectin. The amylose reacts first with iodine despite the fact that it is present in far smaller amounts than amylopectin. The amylose in old starch solutions has undergone partial hydrolysis; on the addition of iodine a blue-violet to red-violet color appears. For analytical work, it is customary to use the so-called soluble starch (Zulkowsky starch),[258] which is prepared by heating starch with glycerin and then precipitating with alcohol. This product contains degraded (depolymerized) starch or degraded amylopectin.[259] Another variety of soluble starch is prepared by grinding starch extremely fine under alcohol.[259a] The resulting product, after drying, readily forms colloidal solutions with water. These dispersions do not flocculate when they are added to solutions containing electrolytes, and hence are well suited for use as indicators in iodometric titrations.

Degraded starch, methylated starch, cellulose swelled by means of zinc chloride, and, as Barger[260] found, numerous low polymer organic compounds also give color reactions with iodine that are analogous to that exhibited by starch. Hence, the iodine-starch reaction, which is employed as the most sensitive test for starch, is not strictly specific. It has been found that all organic substances which react with iodine in a fashion analogous to starch never show this behavior if they are in definitely crystalline form or when molecularly dissolved. The action occurs solely when the materials are in the extremely surface-rich form of the colloidal range. This is reminiscent of the blue coloration of basic lanthanum acetate with iodine (see p. 553), which also is pronounced

[258] K. ZULKOWSKY, *Ber.* **13**, 1395 (1880).

[259] H. PRINGSHEIM and K. WOLFSOHN, *Ber.* **57**, 887 (1924); A. PICTET, *Helv. Chim. Acta* **9**, 33 (1926); **12**, 700 (1929).

[259a] Compare H. A. CONNER and R. W. BOVIK, *Ind. Eng. Chem.* **16**, 772 (1944). Other references will be found there.

[260] G. BARGER and F. G. EATON, *J. Chem. Soc.* **125**, 2407 (1924); compare also M. BERGMANN, *Ber.* **57**, 755 (1924).

only with freshly prepared gel-like preparations. Consequently, there is no doubt that the action involves the extensive surface development of certain materials, but this cannot be the only determinant. Otherwise, gel-like products would give a blue coloration in far more instances than is actually the case. Another factor, which, however, is insufficient of itself, is obviously a content of oxygen atoms in the surface that are active toward iodine. . Probably these oxygen atoms must be present in certain linkages so that they can serve for the coordinative binding of iodine molecules. The binding place for iodine in starch (or its constituents) probably is to be sought in the ether-linked oxygen atoms of the giant molecules of the amylose or amylopectin. However, it cannot be stated whether it is the cyclic bound or the bridge oxygen atoms, as shown in (II) and (III), that are responsible for the binding of the iodine. There is no doubt that the presence of water (probably the hydration of the constituents of the starch) is necessary for the occurrence of the iodine-starch reaction. Dry starch does not react with iodine vapor, and starch colored with iodine solution turns brown when dried, and the blue is only restored when the material is moistened with water. It is now generally accepted that the iodine is adsorbed on the surface of the starch, or that an adsorption compound between iodine and starch (or its constituents) is formed. As is true of all adsorption compounds, the composition of iodine-starch is dependent on the conditions under which it is produced. It should also be noted that starch not only is not a uniform compound, but that, in addition, starch solutions are the object of several processes from the instant of their production. Nevertheless, the studies of Meyer and Bernfeld[261] make it possible to assert several remarkable facts about the product of the starch-iodine reaction. Through colorimetric measurements at various concentrations, they were able to show that several iodine molecules invariably unite with a number of starch molecules in the starch-iodine reaction. Furthermore, they found that blue iodine-amylose solutions, obtained in one case with an excess of iodine, and in another case with an excess of amylose, on treatment with electrolytes, produce blue-black precipitates, which have the approximate compositions $[I_2 \cdot (C_6H_{10}O_5)_{10}]_n$ and $[I_2 \cdot (C_6H_{10}O_5)_{20}]_n$, respectively. Therefore, it appears that giant molecules of amylose are held together by iodine molecules, which are coordinated on definite oxygen atoms. The increase in particle size resulting from such iodine bridging makes it plausible that a flocculation follows the addition of electrolytes, a result which either does not occur at all or only much more slowly in pure amylose solutions. According to the foregoing structures, it can be assumed, at least statistically, that such iodine bridges are

[261] K. H. MEYER and P. BERNFELD, *Helv. Chim. Acta* **24**, 389 (1941).

present at intervals of 5–10 glucose units in the amylose chains. The blue solutions of iodine-starch can be regarded as colloidal solutions of adsorption compounds of iodine with amylose, in which starch (or its constituents) may act as the protective colloid. ·

The adsorptive binding of iodine on starch, which is viewed as coordination of iodine on oxygen atoms, is much firmer than the coordinative binding of iodine on iodide ions in alkali polyiodide solutions. This is shown by the fact that a blue color appears at once when starch is added to concentrated alkali iodide solutions which contain traces of free iodine or I_3^- ions. The production of the blue starch adsorption compound permits the detection of much smaller amounts of iodine than can be revealed by the yellow color of the iodine-iodide ion coordination. According to Kolthoff,[262] the values are: 2.6 mg. I_2/l. against 7.5 mg. I_2/l. in the absence of starch. Here again, there is the customary enhancement of the visibility of one of the constituents of an adsorption compound. The presence of iodide ions undoubtedly plays a role when the iodine-starch reaction is carried out in dilute iodine solutions. Minimal amounts of an iodide ion content must be exceeded before the intensity of the blue color will reach its maximum value.[263] Correspondingly, metal ions (Hg, Ag, Tl) which consume iodide ions, prevent the occurrence of the iodine-starch reaction. The presence of iodide ions must be considered in the colorimetric determination of small amounts of iodine by means of the starch reaction.[264]

The precipitates formed by the action of proteins with heteropolyacids (phosphomolybdic, phosphotungstic, *etc.*) are· inorganic-organic adsorption compounds with a colloidal organic component as adsorbent. The reactivity of amido groups on the surface of colloidal protein particles is involved in these reactions. All complex acids that are precipitants for proteins are likewise sensitive precipitating agents for alkaloids. This characteristic is used for the general detection and isolation of alkaloids. The variation of the composition with the precipitation conditions makes it probable that many of the precipitates formed by treating alkaloids with complex acids are to be regarded as adsorption compounds whose production involves colloidal alkaloid particles (derived from the hydrolysis of alkaloid salt solutions). However, formula-pure salts of alkaloids with complex acids are known, and presumably these can be made the basis of gravimetric or titrimetric procedures for determining alkaloids. An interesting instance of the analytical application of the production of formula-pure alkaloid salts of

[262] I. M. KOLTHOFF, *Pharm. Weekblad* **156**, 7 (1919).
[263] I. M. KOLTHOFF, *loc. cit.*
[264] Compare H. Q. WOODWARD, *Ind. Eng. Chem., Anal. Ed.* **6**, 331 (1934).

heteropolyacids was provided by Davies and Morgan.[265] They determined small amounts of germanium by converting it into germanomolybdic acid, and then this was precipitated by treatment with cinchonine nitrate. The precipitate after drying at 160°C. has the composition $(C_{19}H_{22}ON_2)_4 \cdot H_4[GeO_4 \cdot 12MoO_3]$, whose germanium content is only 2.38%.

Purely organic adsorption compounds conform to the requirement that at least one participant in their formation must be in the colloidal state at the time, and that they ordinarily result from a surface reaction. In these respects they fall into the same pattern as the purely inorganic and the mixed inorganic-organic adsorption compounds that have already been discussed. Haller[266] has studied extensively the precipitation of adsorption compounds resulting from the union of solutions of polyatomic acid and basic dyes. He found that the composition of the precipitates does not correspond to the anticipated formula of the binary salts but varies within wide limits. Haller assumes that the products are adsorption compounds produced by combination of colloidal particles of one of the dyes with molecules or colloidal particles of the other. According to the viewpoint accepted by the present writer, these products represent salt-bindings on the surface of colloidal particles of the dye, without the development of salts in an individual, separate phase. Basic dyes can be precipitated from aqueous solution or solutions of their salts by the addition of tannin. The products are called tannin-color lakes. This action is the basis of the tannin-mordant dyeing of textiles. It was pointed out in connection with the tannin-metal precipitates that phenolic groups on the surface of tannin particles react with metal ions or with metal-containing colloidal particles formed by hydrolysis. The formation of the adsorption compounds between dyes and tannin is likewise due to surface reactions of phenol groups of tannin. The production of a dye-tannin adsorption compound was recommended for the determination of tannin.[267] The products of the rather sensitive precipitations of proteins with tannin belong among the purely organic adsorption compounds. They surely involve the union of colloidal particles of both components, with NH_2 and OH groups as binding positions. Alkaloids can also be precipitated with tannin; these adsorption compounds seem to differ with respect to their resistance to acids.[268] A familiar method of removing proteins from biological fluids is to precipi-

[265] G. R. DAVIES and G. MORGAN, *Analyst* **63**, 388 (1938).

[266] R. HALLER, *Kolloid-Z.* **22**, 113 (1918); **24**, 56 (1919); **27**, 20 (1920).

[267] H. TRETZMÜLLER, *Chem. Abstracts* **30**, 4353 (1936).

[268] Compare H. I. A. HENRY, in Allen's Commercial Organic Analysis, Vol. VII, p. 25. Philadelphia, 1929.

tate them with sulfosalicylic acid. This precipitate is certainly to be viewed as a purely organic adsorption compound. The same holds for the precipitation of proteins and alkaloids with bis-*p*-chlorophenyl phosphoric acid (see Chapter VI).

All previous experience with the analytical application of the formation of adsorption compounds has proved very satisfactory, particularly with respect to the great sensitivity of the respective precipitation reactions. The selectivity is often not as satisfactory, but this characteristic can frequently be improved through the judicious use of masking agents and the maintenance of certain pH values. Because of the dependence of their composition on the precipitation conditions, adsorption compounds can never be used as the final weighing form in gravimetric methods. They can serve only as collector or separating forms which, after being isolated, can be converted into formula-pure products by subsequent operations. However, adsorption compounds formed within lower concentration regions can serve as the basis of colorimetric or nephelometric methods. The outstanding characteristic of all adsorption compounds and a weighty indication as to the possibility of their being formed is the colloidal state of at least one of the components at the time of the formation process. This process, therefore, is always localized on the surface of the colloidal particles, and does not progress completely toward the interior of the particles. Reactions, which have a definite reaction *locale* are known as topochemical reactions. The formation of all adsorption compounds, as well as all adsorption processes in which chemical bindings, in the widest sense, play a part, accordingly should be included among topochemical reactions. The analytical importance of topochemical reactions is discussed, in other connections, in Chapter XI.

Isolation and Separation of Materials by Adsorption (Adsorption Analysis)

The term "adsorption" signifies the accumulation of a material on the surface of a second material. It has been repeatedly stressed at various places in this text, and demonstrated by appropriate illustrations, that this phenomenon proceeds to quite variable extents and that the action is quite selective. Hence, it may be expected that dissolved, or colloidally dispersed, materials can be quantitatively fixed on the surface of properly chosen adsorbents and thus separated from the solvent[269] or dispersion medium, or perhaps from cosolutes. In fact, instances of the

[269] In the strict sense, this should read "from the bulk of the solvent," since solvent as well as solute is invariably fixed on the surface of an adsorbent when dissolved materials are adsorbed.

isolation of materials by means of adsorption were pointed out in the discussion of induced precipitations, in many of the examples of trace collecting, and likewise in the preceding section, where the characteristic adsorption phenomena were stressed.

The principle of isolating and separating materials by means of adsorption is applied systematically in "adsorption analysis." In a strict sense this designation is not correct, because, in chemistry, analysis denotes exclusively the detection or quantitative determination of materials. Neither of these objectives can be accomplished by adsorption, *per se*, except in a few special cases. It can only bring about the separation of materials. The designation "analysis" doubtless arose from the fact that, in the beginning, adsorptive separations were carried out on mixtures of dyestuffs or colored compounds, and in such cases the distinctive self-colors of the separated cosolutes can actually also serve as a means of detection. Later, adsorptive separation was extended to colorless materials and its major importance now lies in this field. Physical or chemical tests are of course indispensable for the actual identification of the individual colorless components of mixtures that have been separated by this procedure. Accordingly, the so-called adsorption analysis is in reality only one step in the chemical analytical procedure, and bears about the same relation to the total operation as do precipitation, filtration, extraction, distillation, *etc.* However, this partial operation in many cases is far more important than the actual identification. It has been found that selective adsorption not only can bring about a local accumulation of traces of a material which facilitates the subsequent identification but actually, in some cases, the latter operation is made possible only because of this localization. Of still more significance is the fact that adsorption separations succeed in certain cases, where other methods have been found impossible or where the separations have been accomplished only by much more tedious procedures. There is a direct relation here between adsorption and specificity, a very important analytical factor.

Three types of adsorption analysis are used. They are distinguished by the nature of the adsorbing surfaces. The first is *capillary analysis* (F. Goppelsroeder) in which filter paper serves as adsorbent. The second type is *chromatography* (M. Tswett), which usually employs pulverized mineral adsorbents. The third is *foaming analysis* (Wo. Ostwald), in which previously dissolved materials are fixed on the surface of a foam. *Spot test analysis*, which has now been developed into a special analytical method, had its genesis in capillary analysis. The more important effects which are related to capillarity and adsorption and that play a role in spot test analysis will be discussed in connection with capillary analysis.

Capillary Analysis and Capillary Effects in Spot Test Analysis

The fact that materials dissolved in water are retained to varying extents by filter paper was among the first adsorption effects to be recognized. Consequently, quite a few early workers sought to make analytical use of this type of adsorption. Schönbein and Goppelsroeder were especially prominent among these pioneers.

Schönbein[270] was the first to show that the water travels ahead of the solutes when aqueous solutions rise in filter paper, and he also found that the relative heights reached vary from solute to solute. Hence he found it possible to detect some individual components in solutions of mixtures of certain salts or dyes by allowing them to ascend filter paper. He was also the first to foresee the analytical significance of the capillary pictures obtained in filter paper by this procedure.[271]

Goppelsroeder, one of Schönbein's students, spent many years (1861–1910) in thorough investigations of this topic. He collected a large mass of statistical material on the heights and rates of ascent of organic liquids, and solutions of organic compounds, in strips of filter paper and other fibrous capillary media. He demonstrated that the characteristic data furnished by these systems are dependent on the nature of the solutes, their concentration, the capillary medium, the temperature, and the period of the capillary rise.[272] He not only studied capillary spreading and adsorption as such, but he also considered their analytical employment as an important objective.[273] His most impressive and deservedly famous finding was the detection of $0.000,025\gamma$ of methylene blue. He accomplished this feat by allowing 1 ml. of approximately 1:40,000,000,-000 dye solution to rise by capillarity and obtained a faint, but nevertheless recognizable, adsorption zone of methylene blue on the filter paper. This extreme instance, which has never been equalled, serves to demonstrate the great importance of adsorption in the localized fixation of traces of dissolved materials on solid surfaces. In other important

[270] F. SCHÖNBEIN, *Ann.* **114**, 275 (1861).

[271] F. SCHÖNBEIN [*Verh. Naturf. Ges. Basel* **3**, 249 (1861)] remarked prophetically that the principle used by him "might render service to the analytical chemist as a qualitative method of investigation in those cases where other reagents leave him in the lurch." Subsequent findings and especially chromatographic analysis (see p. 589), which likewise is based on adsorption, have beautifully confirmed Schönbein's predictions.

[272] A bibliography of Goppelsroeder's many publications is contained in the excellent and critical monograph by H. RHEINBOLDT, "Kapillar und Adsorptionsanalyse" in J. Houben, Die Methoden der organischen Chemie, 3rd ed., Vol. 1, p. 291. Leipzig, 1935.

[273] Compare F. GOPPELSROEDER, Kapillaranalyse, Dresden, 1910.

studies he dealt with dissolved mixtures of basic and acid dyes. When these solutions were allowed to rise by capillary action, the dyes formed distinct adsorption zones on the filter paper. He also investigated the capillary rise in filter paper of solutions of alkaloids, pharmaceutical products, foods and condiments. He coined the term "capillary analysis"[274] for the analytical utilization of the capillary pictures produced by the spreading through filter paper of liquids or solutions.

There have been many practical applications of capillary analysis, especially in the examination and testing of dyes and drugs. In the past few years this procedure has been replaced extensively by chromatographic analysis (see p. 589) which in principle is similar to capillary analysis. Goppelsroeder gave little attention to the behavior of solutions of inorganic materials when they underwent capillary spreading on paper. Such studies by other investigators will be briefly reviewed in the following paragraphs.

[274] This term, which has now been generally adopted, is poorly chosen because a much too exclusive form of capillary action is thus stressed. There is no doubt that capillary forces participate in the rise and spreading of liquids in the capillaries of filter paper. It should be noted that filter paper possesses two distinct types of capillary spaces; namely, the relatively large interstices (pores) between the cellulose fibers, and the extremely fine capillaries of each individual fiber. The former, because of the low frictional resistance, are principally responsible for the speed with which liquids spread on paper. Because of the walls, which surround both these types of empty spaces, the paper functions not only as the capillary medium but invariably also as the adsorption medium. Obviously, the finer the capillaries the greater the role they will play in adsorption, because here there is a particularly high ratio between the adsorbing surfaces and the liquid which bathes them. Consequently, in capillary analysis consideration must always be given to the simultaneous activity of capillarity and adsorption. Capillarity is dominant in the rise of pure liquids in filter paper as studied by Goppelsroeder, though an adsorption on the surface of the cellulose also occurs in such instances. Consequently, paper is not a suitable medium for a true capillary analysis, i.e., for an exclusive utilization of capillarity. However, true capillary analysis does exist. The outstanding instance is a method of J. TRAUBE [compare Z. anal. Chem. 55, 138 (1916)] who makes use of the dripping of liquids and solutions from glass capillaries. This procedure involves the fact that the volume of a drop, as well as the height of capillary rise, is a measure of the surface tension of the particular liquid or solution. (The larger the drop, the greater the surface tension.) The stalagmometer, introduced by Traube, does not measure the volume of the drop itself, but its reciprocal, i.e., the number of drops obtained when a given volume of liquid flows, not too rapidly, from a capillary. Therefore, the number of drops is inversely proportional to the height of capillary rise, and a lowering of the surface tension of a liquid by the materials dissolved in it is revealed by an increase in the number of drops. Traube showed that even small quantities of capillary-active materials increase the number of drops so greatly that quantitative determinations become feasible. The reference system is the number of drops delivered when a known volume of the pure solvent is discharged from the stalagmometer. (Compare H. RHEINBOLDT, loc. cit. regarding practical applications of this type of analysis.)

Bayley[275] likewise observed the ability of filter paper to adsorb selectively water and every material dissolved in it. He departed from the method of Schönbein and Goppelsroeder who permitted the solution to rise in strips of filter paper; instead, he allowed drops of the solution to spread on paper. Rings of water (solvent) and of more concentrated solution resulted. Bayley showed that this phenomenon depends on the concentration and nature of the dissolved material, as well as on the type of paper employed. He indicated that these observations could serve as the basis of a method for detecting cadmium in the presence of copper.

Lloyd[276] studied the capillary rise of solutions that contained one or more solutes. He found that solutions of single materials developed two consecutive zones on the filter paper. The lower zone contains solute plus water; the upper zone consists entirely of water. The dilution of the solution determines the relative width of the zones; the more dilute the solution, the wider the water zone. With multiple solutions, the heights of ascent, i.e., the traversed zones, are those characteristic of the individual cosolutes, provided certain concentration relationships are not exceeded. Lloyd also found that dilute sulfuric acid undergoes separation into more concentrated acid and pure water when it rises in strips of filter paper.

Fischer and Schmidmer[277] also carried out experiments on the capillary ascent of solutions in filter paper, and discussed the capillary separation of the constituents of solutions. They believed that such separations are due primarily to differences in the diffusion rates of the components.

Reed[278] allowed drops of salt solutions to spread in filter paper and proved that dilute solutions produce a fleck whose outer ring consists of pure water. The width of this water ring increases with the dilution and reaches a limiting value. In other words, there is a dilution beyond which the width of the water ring stays constant. Drops of dilute sulfuric acid also undergo this capillary separation when they are placed on paper. Reed likewise studied the behavior of solutions containing several salts. They form definite zones and the constituents of the solution travel within these. There is joint movement at first, i.e., the zones traversed by the various ingredients of the solution overlap. Isolation of one of the cosolutes from the others occurs only in the outermost zone, which is surrounded by pure water.

Trey[279] was the first to show that it is possible, in the systematic

[275] TH. BAYLEY, J. Chem. Soc. 33 I, 304 (1878).

[276] J. U. LLOYD, Chem. News 51, 51 (1885).

[277] E. FISCHER and E. SCHMIDMER, Ann. 272, 156 (1892).

[278] L. REED, Chem. News 67, 261 (1893); compare also J. Chem. Soc., Abstr. Proc. VIII-IX, 123 (1892-93).

[279] H. TREY, Z. anal. Chem. 37, 743 (1898).

scheme of analysis, to detect two elements in the presence of each other by means of adsorption. He accomplished the separation of copper from cadmium which Bayley (*loc. cit.*) had already suggested. Trey likewise used the drop method, and described a simple apparatus for bringing small drops onto a filter paper. In an ammoniacal solution containing copper and cadmium, the $Cd(NH_3)_4^{++}$, together with the water, precedes the $Cu(NH_3)_4^{++}$, and, after development over $(NH_4)_2S$, can be recognized by a yellow border around the black CuS ring. However, the method succeeds only at great dilution and at low concentrations of copper.

Holmgren[280] was the first to study the previously known fact that the height of ascent depends on the concentration. He likewise used the more rapid drop method, and investigated the behavior of dilute acid solutions. He determined the quantitative relationships between the central ring of the acid spot and the concentric water ring and also of the concentration of the acid, and, by setting up a constant for the paper, was able to state a simple formula by which the concentration of very dilute acids could be determined from these values. He pointed out that the nature of the paper is of importance in this form of capillary analysis.

Skraup and his coworkers,[281] stimulated by these studies, made extensive investigations of the heights to which solutions of salts rose in filter paper. They determined a relationship to various chemical and physical factors, such as dissociation and hydrolysis, as well as the temperature of the solution and the ash content of the paper. Salts can be placed in two classes that are rather directly opposed to each other with respect to their behavior toward filter paper. The first class contains the alkali and alkaline earth salts, the second category consists of the heavy metal and aluminum salts and also complex salts. While the salts of the first class, in aqueous solutions, rise almost as high as the solvent and are independent of the concentration with respect to height of ascent and adsorption, those of the second class do not rise nearly as high as water, and the height decreases with increasing dilution. Cations of a similar nature rise to about the same height; this is shown particularly in the $(NH_4)_2S$ group, by the Fe^{+++} and Al^{+++} ions.

Krulla[282] studied the adsorption phenomena of the rise of salts in filter paper, and experimented with single solutions and mixtures of salts (filter strip method). The adsorbability of the individual components is not interfered with in solutions of mixtures of salts of different ions;

[280] J. HOLMGREN, *Biochem. Z.* **14**, 187 (1908); compare also H. SCHMIDT, *Kolloid-Z.* **13**, 146 (1913).

[281] Z. SKRAUP, A. v. BIEHLER, R. LANG, E. PHILIPPI and I. PRINGLINGER, *Monatsh.* **31**, 1067 (1910).

[282] R. KRULLA, *Z. physik. Chem.* **66**, 307 (1909).

consequently, these rise in filter paper just as high as though they were present alone. However, the addition of the common ion causes an increase of the adsorbability of the particular ion, and so decreases the height of ascent. This observation, that doubtless is connected with dissociation, was used by Krulla for the qualitative detection of ions. Different ions are added to the solution being tested for an ion until one is found that brings about a distinct lowering of the height of ascent. The ion that causes this, was the one in the solution. There is also a relation, on the one hand, between the kind of paper and the nature and concentration of the dissolved material, and the height of ascent of the solvent and of the solute, on the other. Krulla worked out a formula expressing these relationships; it makes possible, in principle, the qualitative detection or the quantitative determination of a salt in a pure solution. If the concentration is known, the experimentally determined heights of ascent can be inserted in the formula, and constants can then be calculated that are characteristic for the various salts and can be used for their qualitative detection. The percentage content of a solution can also be determined if the solute, and therefore its constant, is known, by substituting this value and the observed height of ascent in the formula. These interesting findings may possibly be utilized for rapid quantitative determinations and for the qualitative detection of organic materials, particularly dyes, but they have practically no value for the analysis of inorganic materials.

The foregoing studies show:

1. The rise of solutions in filter paper and the spreading of drops of a solution on paper can bring about an accumulation of the solute in certain zones of the paper. Capillarity and adsorption phenomena are the causes of this separation.

2. Filter paper exhibits selective adsorption toward dissolved materials; consequently, they travel in paper to varying degrees. Water migrates in the capillaries of the paper, some of it just as far as, some of it farther than, the materials dissolved in it.

3. The size of the water rings or the zones formed by the capillary separation of the solvent and the solutes depends on the concentration of the solution; the more dilute the solution, the larger the rings or zones.

4. A capillary separation of the solvent and the dissolved material is successful only in very dilute solutions.

5. Heights and times of ascent depend on the nature of the solute, as well as on the concentration.

6. Chemically similar materials in equal molar concentrations rise to approximately the same height.

7. Extensive differences in the heights of ascent, that can be used for

analytical purposes, are often observed in the case of dyes and organic compounds, but rarely with inorganic salts.

8. A quantitative separation of the components of a solution of a mixture is never accomplished. A dissolved material is isolated only if it moves in the outermost zone. In all the other parts of the paper through which a solution has passed, all of the components are present in varying quantities.

9. The adsorbability of one ionic species of an electrolyte is increased by large amounts of common ions.

10. Solutions of mixtures of salts furnishing different ions do not impair the adsorption of the individual components. So far as is now known, this statement holds only in the absence of more strongly adsorbed ions (displacement adsorption).

This compilation shows that the separative action of filter paper, due to capillary phenomena, is, as a rule, insufficient to effect an isolation of the inorganic components of a solution into separate distinct zones. Even in favorable cases, *i.e.*, when the concentration relationships make a formation of zones possible, the individual components in these zones must still be revealed by characteristic reactions, since they are not present alone and in the pure state, but are accompanied by varying amounts of their cosolutes. This limitation is not particularly encouraging, but nevertheless the results of the capillary analytical studies cited in the foregoing discussion, taken together with isolated observations of the reaction picture of qualitative tests on filter paper, provided information that was important to the development of a semimicro and micro analytical technic that is now known as spot test analysis. In the literal sense, spot test analysis consists of the application and judicious extension of the principle of accomplishing a chemical reaction within the volume of one or two drops on a porous surface, preferably filter paper. The term "spot test" has, however, been commonly adopted for the procedure of carrying out tests within drops on non-porous substrates (spot plate, glass, *etc.*), even though the term "drop test" would be more correct for this technic. Spot reactions carried out on filter paper offer extensive opportunities for the utilization of adsorption and capillarity phenomena in the separation of materials and also in planned efforts to enhance the selectivity and sensitivity of tests. Several points concerning these objectives are discussed in the following paragraphs.

In the first place, when spot tests are made on filter paper by bringing together one drop each of the test and reagent solutions, the fundamental chemical reaction occurs in the plane of the paper, so to speak. If insoluble reaction products result, they are held fast by the paper after a certain particle size is reached, while the excess reagent solution, together

with any nonreacting cosolutes, pass on through the capillaries of the paper. The consequence is a microprecipitation and a microfiltration in the paper moistened by the drops of the liquid. Because of the contrast and direct contact with the white substratum, colored precipitates that remain behind as the "flecks" are much more visible than the same amount of precipitate suspended in the corresponding volume of liquid in a glass vessel. The effect discussed on p. 438 comes into play here, *i.e.*, the fact that the tinting of a colorless solid of a given particle size (in this case the paper capillaries) is more marked the smaller the particles of the colored enveloping solid. When reactions lead to insoluble products, an opportunity is afforded, during the aggregation of the particles of the precipitate, for an envelopment of the capillaries of the paper[283] by particularly fine particles.

The intensity and size of a fleck produced by a precipitation reaction on paper depend on a number of factors. Among these are: the quantity, color, and form-species of the precipitate; the order in which the drops of the reacting solutions are applied; the particular size of the drops (which may range between 0.001 and 0.05 ml.); and the quality of the paper, which preferably should have excellent adsorbing powers. As a rule, precipitation reactions are best made on thick filter paper, which, though it has good absorptivity, nevertheless does not permit a drop of liquid to be soaked up immediately by capillary spreading, but instead (even though temporarily) permits the liquid to form a globule on the paper. When spot tests are made on such papers by successively applying single drops of the appropriate solutions, the reaction occurs before the drops are completely absorbed. The flecks are then smaller and more distinct than those obtained on thinner papers. The latter take up the liquid more rapidly, and hence, because of the rapid capillary spreading, the first drop is completely absorbed before the second drop can be applied. The favorable effect of a suitable variety of paper is shown nicely by the spot test for cadmium with [Fe(α,α'-dip)$_3$]I$_2$ solution in which a violet precipitate of [Fe(α,α'-dip)3][CdI$_4$] is formed (see p. 324). The reaction is more sensitive by powers of ten when carried out on spot test paper (S. & S. 601) rather than on a spot plate. When a spot reaction produces only a small quantity of a precipitate, the latter is frequently retained so tenaciously by the capillaries of the paper that, at most, only minute quantities are dislodged when drops of water are subsequently applied. Thus, the flecks may be washed, and are made more discernible by such removal of any excess of colored reagent solutions. If spot reactions result in colored, soluble products, they too are

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[283] H. Bechhold, *Z. physik. Chem.* **64,** 328 (1908) states that the maximum pore size of good quality filter paper is about 0.03 mm.

localized within the bounds of a fleck, and can be easily seen because of the contrast with the white paper. It should be noted that flecks formed by small amounts of a precipitate usually cannot be distinguished directly from those due to colored soluble products.[284] .The reason is that the fine state of subdivision of the precipitate is preserved by its adhesion to the paper, and hence extensive aggregation of the particles is prevented or greatly retarded. This fact is quite important with respect to the reactivity of solids that are highly dispersed in paper, a topic to be discussed later.

The foregoing discussion has dealt with several general phenomena that attend spot reactions which produce precipitates. Certain ˙details of the structure and appearance of flecks are important. These morphological characteristics are closely related to the capillary and adsorptive action of the paper. There are three typical forms of flecks which may develop on a given kind of paper, dependent on the quantity of the colored precipitate: (a) A central circular fleck, often with jagged edges, surrounded by a water ring of varying width; (b) A central circular fleck, which contains more precipitate in its outer than in its central portion. This condition is sometimes directly discernible because of the difference in color intensities; (c) No central colored circle; instead only a moist area showing no distinct precipitate formation, enclosed by a colored ring, which, in turn, is surrounded by a water ring. These three fleck pictures are extreme cases and continuous gradations into each other are possible. The development of the different types is often due to the adsorption of dissolved materials when a drop of the solution is spread through the paper. The behavior of solutions of dyes clearly reveals some of the details of this adsorption. Some, like eosin, an acid dye, are only slightly adsorbed by paper. In such cases, practically the entire moistened area is tinted uniformly when a drop of the dye solution is applied to the paper. Others, such as the basic dye methylene blue, are strongly adsorbed and the dye then accumulates on the inside of the zone moistened by the spreading drop. According to the concentration, such dyes produce either a central circular colored spot or a colored ring, surrounded by a water ring of varying width. Both the ring and the round fleck are due to the adsorption of the dye by the paper. The outer colorless water ring corresponds to a colorless filtrate, such as is obtained after a solution of methylene blue has been shaken with charcoal. In both instances, the disappearance of the color proves that the dye has been completely adsorbed. A special explanation is necessary if an annular adsorption zone of the dye develops when a drop of a dilute solution of

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[284] Usually, a differentiation is possible by adding a drop of water to the fleck. The soluble colored material is thus ordinarily caused to undergo capillary migration.

a strongly adsorbable dye is placed on paper. When this happens, the surprising fact is that a central zone is obtained, in which only a little, or sometimes no dye at all, is adsorbed. This can be ascribed to the competition between the water and the dissolved dye for the paper which is acting as adsorbent. The water is taken up more rapidly and so wins out; in other words, a negative adsorption occurs first. The colored ring represents the region of positive adsorption; its inner edge indicates the beginning and its outer edge the end of the adsorption. The positive adsorption of the dye results because the liquid in the zone of the paper farthest removed from the point of application of the drop moves away more slowly through the capillary spaces of the paper. This gradually sets up the conditions necessary to the establishment of adsorption equilibria from dilute solutions. Consequently, the end effect is a positive adsorption of strongly adsorbable dyes, as was to be expected, in which all of the dye is held fast in a ring zone. The negative adsorption is a partial process, whose effect becomes visible through the development of a central colorless water zone when the solution passes through the paper which acts as adsorbent. Analogous capillary pictures or, more correctly, adsorption pictures, such as can be observed directly with solutions of dyes, may be assumed also for salt solutions when a drop of the latter is placed on filter paper and allowed to spread by capillarity. If the fleck is then spotted with a drop of a reagent solution, reaction takes place in those areas where there has been a previous localization due to adsorption. Colored reaction products will, accordingly, reveal the hitherto invisible adsorption zones (circles or rings). However, the adsorption zones do not always become sharply visible after the reaction occurs. There may be displacements, or the zones may be more or less defective because a reagent solution, in its passage through the moist paper, may, just like pure water, remove loosely adsorbed materials from the paper and drive them ahead of itself. In such cases, a reaction occurs during this displacement. The phenomenon that water-soluble salts in porous materials can likewise be pushed ahead by capillary-driven water was studied by Liesegang and Watanabe.[285] This effect is shown especially well if water is applied to dry filter paper impregnated with salt solutions, but it also is exhibited by moist paper. The movement of materials by the so-called Bechhold capillary phenomenon[286] is a quite similar effect. This term is applied to the fact that when porous materials are soaked with salt solutions and then dried, the salts accumulate in the outer layers. In paper, the accumulation is accordingly on the surface and at the edges. The reason for this effect is that the

[285] R. E. LIESEGANG and M. WATANABE, *Kolloid-Z.* **32**, 177 (1923).

[286] H. BECHHOLD, *Kolloid-Z.* **27**, 229 (1920).

solvent evaporated on the surface is replaced by solution drawn thither by capillary action. This capillary movement of salt in the direction of the volatilization of a solvent is also the reason why the solute accumulates on the heated side of a piece of filter paper that has been spotted with a drop of a salt solution and then warmed unilaterally. The following experiment demonstrates this effect nicely. Two pieces of filter paper are spotted with single drops of a salt solution. One piece is allowed to dry gradually from both sides in the air; the other is placed on a glass plate and dried rapidly by heating from above. Then both papers are spotted with a suitable reagent solution. The fleck is much more distinct on the second paper. Hence, localized enrichments of material can be secured by warming spotted areas and in this way the sensitivity of spot reactions may be increased considerably. The favorable effect of one-sided warming is especially evident in spot reactions made on thick paper. This is understandable if it is remembered that the capillary spreading of a drop of solution proceeds in all directions in paper, *i.e.*, not only along the surface but also toward the interior. In thin paper, the capillary spreading and the concurrent adsorption take place almost entirely in the surface; in thick paper the adsorption in the interior also plays a role. The consequence of the depth and surface adsorption is that the intensity of a fleck, produced by not too small quantities of a precipitate, is almost equal on both sides of a thin paper, whereas very considerable differences may appear if thick paper is used. Consequently, spot reactions with very dilute solutions often produce no visible fleck on the underside of a thick paper, aside from a moisture stain due to the water that has moved away through the capillaries both before and after the reaction.

Among the factors that may contribute to the morphology of a fleck is also the behavior of filter paper toward colloidal solutions. Observations and studies along this line are due to Fichter and Sahlbohm.[287] They showed that, when strips of filter paper are dipped into hydrophobic sols, negative sols rise as far as the water ascends, whereas positive sols travel only a short distance above the level of the solution and then coagulate to gels. This same distinction in capillary behavior can be observed if drops of positive or negative sols are placed on filter paper. Sahlbohm explained the phenomenon as an electrocoagulation process. It provides the basis of an interesting rapid method of determining the sign of the charged particles of a sol. Obviously, the behavior of filter paper toward colloidal solutions is of significance with respect to the

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[287] F. Fichter and N. Sahlbohm, *Verh. Naturf. Ges. Basel* **12**, 1 (1910); *Kolloidchem. Beihefte* **2**, 132 (1910); *Kolloid-Z.* **8**, 1 (1911); compare also T. Malarski, *ibid.* **23**, 113 (1918); A. Boutaric, *Compt. rend.* **198**, 551, 2247 (1934).

fleck picture of spot reactions because one of the stages in the formation of a precipitate invariably is a colloidal dispersion, and very stable hydrosols are often produced when precipitations are made from very dilute solutions. The paper may have a direct influence here by discharging and coagulating hydrosols in definite zones of the fleck. When dealing with colloidally dispersed precipitates that are not coagulated by paper, and with those that undergo a gradual aggregation by electrolytes, it must be noted that, at first, the colloidal particles are carried along with the water that is moving away from the scene of the reaction. This transport continues until aggregation produces particles of such size that further movement is halted. Hence, it is clear that the deposition of the particles of a precipitate in the form of rings, or the accumulation of precipitates on the periphery of round flecks, can also be brought about by changes in state of colloidal dispersions. Consequently, a precipitate produced by a spot reaction does not necessarily separate at the actual site of the reaction.

Inspection of the capillary picture obtained by placing a drop of methylene blue solution on filter paper (see p. 576) showed that adsorption resulted in a localization of the dye in definite circular or ring shaped zones of the paper. Analogous local accumulation of material can be noted in the capillary spreading of dilute solutions of hydrolyzable salts and acids in indicator papers.[288] For example, a drop of dilute ammonium acetate solution turns both blue and red litmus paper violet. Closer examination, however, reveals that the center of the fleck is more blue, and its edges are redder. The reason is that the ammonia produced by the hydrolysis is more strongly adsorbed by the paper than the acetic acid, and in both adsorption zones there is direct reaction by the corresponding H^+ and OH^- ions with the indicator. The adsorption picture of hydrolysis products is seen more plainly when a drop of lead acetate solution is applied to litmus paper. A blue ring appears at some distance from the center of the fleck; it is due to the adsorption of basic lead hydroxide. The acetic acid proceeds onward through capillary action, and only gives an indicator change, in the form of a red ring, still further out. The spot picture of very dilute acids on indicator papers is quite enlightening. If, for example, a drop of 0.001 N hydrochloric acid is placed on Congo paper, the center of the moist fleck remains unchanged, i.e., it stays red. An indicator change due to the action of H^+ ions is revealed in the form of a narrow blue ring that surrounds the central area and the blue ring in turn is encircled by a wide water ring. Dimethyl yellow, azolitmin, litmus, and other test papers, show these same annular

[288] Compare I. M. KOLTHOFF, Acid-Base Indicators (translated by C. Rosenblum), p. 373. New York, 1937.

zones of indicator color changes.   In all cases, the relative radii of the water and the acid circles on the indicator paper are dependent on the original concentration of the acid.[289]   The annular color change zone produced on an indicator paper by very dilute acids is an adsorption picture; in all respects it is analogous to the annular adsorption zone formed by dilute methylene blue solution on plain filter paper.   The following explanation seems plausible.   When a drop of dilute acid is placed on an indicator paper and spreads, at first only water is adsorbed (central water circle).   Accordingly, this zone again corresponds to a negative adsorption that precedes the subsequent positive adsorption. Because of the slower advance, H^+ ions are adsorbed from the acid solution that is moving outward by capillary action, and thus the indicator is changed (annular zone of the color change).   After the acid is consumed, water alone continues to spread outward (outer water ring).[290] Here again is exhibited the interesting effect of the localization of practically all of the acid in a small adsorption zone, whereas the water distributes itself fairly uniformly over the entire fleck, which in some instances represents an incomparably larger area.   There is no other known procedure for attaining such extensive concentration so quickly and simply.   It is hardly necessary to emphasize the analytical value of this means of localizing material, which is by no means limited to acids, but occurs also with other readily adsorbed compounds or their ions.

The foregoing discussion of the spot pictures on indicator papers forms a good preface to the consideration of a very important technic in spot testing, namely, the use of papers impregnated with suitable reagents.   The description of spot reactions carried out on indicator papers makes it apparent that capillary spreading and adsorption play a role in reagent papers also.   The use of papers containing water-insoluble reactants is of great importance.   When such papers are employed in spot tests, finely divided solids undergo reactions with dissolved materials, and great advantages may result.   In the first place, dilution, which necessarily occurs when drops of the test and reagent solutions are brought together, is avoided.   In addition, there is no shifting of materials by diffusion processes, which so often distort the capillary picture of adsorbed compounds.   Furthermore, papers impregnated with solid

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[289] Compare K. Prosad and B. N. Gosch, *Kolloid-Z.* **84**, 275 (1938); H. Schmidt, *ibid.* **13**, 146 (1913); **24**, 49 (1919); J. Holmgren, *loc. cit.*

[290] Heretofore, the capillary phenomena attending the spotting of dilute acids on indicator papers were ascribed to differences in the diffusion velocity of water and H^+ ions (compare I. M. Kolthoff, *loc. cit.*, p. 374).   According to the interpretation given here, adsorption is the chief factor.

reagents do not permit diffusion in the interior which of course may decrease the sensitivity of a test.   A reaction on an impregnated paper occurs directly on the surface of a solid reagent which is always present in excess; more sharply defined flecks result.   A fact of considerable importance is that by varying the degree of impregnation of a paper, it is often possible to set up conditions under which a reaction will reveal even minute amounts of material, provided the reaction produces a characteristic color change.   In some cases, no trace of a reaction can be seen in a test tube but, because of the advantages just cited, the change can be perceived clearly and directly if the test is carried out as a spot reaction.   Several typical examples will emphasize this important fact. If filter paper is bathed in permanganate solution, the cellulose is partly oxidized and manganese dioxide is deposited in the pores of the paper. The color of the impregnated paper ranges from light yellow to brown, according to the concentration of the permanganate solution.   When the test paper is treated with a drop of a dilute solution of a reducing agent, such as oxalic or sulfurous acids, the MnO_2 is reduced to a colorless manganous salt, and a lighter, even white, fleck appears.   Reducing agents, in quantities approximating as little as 1γ, can be detected in this way.[291]   A similar spot test for hydrogen peroxide was developed by Kempf.[292]   It is based on the reaction: $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$. When a drop of peroxide solution is placed on paper impregnated with lead sulfide, a white spot or ring develops, depending on the concentration of the peroxide and the strength of the impregnation.   Because of the distinct contrast with the dark background, the identification limit of this test is 0.04γ H_2O_2.   Of course, MnO_2 can be reduced, or PbS can be oxidized, in a test tube, but then the reactions are absolutely useless for the detection of small amounts of reducing materials or hydrogen peroxide.   They can be utilized for qualitative analytical purposes only when conducted as spot reactions on paper.   The following two instances are especially interesting because, when the reactions were carried out on reagent paper, they led to the discovery of hitherto unknown compounds. Feigl and Braile[293] studied the action of an alkali polysulfide solution when a drop was placed on thallous sulfide paper and the fleck then treated with dilute acid or hydrogen peroxide.   Thallous sulfide ordinarily dissolves readily in acids, hence the black paper lost its color. However, a red-brown fleck was left where the drop had been applied. The same result is obtained if a drop of a carbon bisulfide solution of sulfur is placed on the thallous sulfide paper.   When a solution of selenium

[291] F. Feigl and R. Uzel, *Mikrochemie* **19**, 136 (1936).
[292] R. Kempf, *Z. anal. Chem.* **89**, 88 (1933).
[293] F. Feigl and N. Braile, *Chemist-Analyst* **33**, 28 (1944).

in carbon bisulfide is used, a dark brown fleck remains after the treatment with acid or peroxide.   These effects, which will reveal 1γ of Se or 3γ of S per drop, probably are due to the formation of adsorption compounds between thallous sulfide and sulfur or selenium, or thallium polysulfide or thallium selenosulfide may be produced.   The existence of such acid-resistant thallium compounds had not been known before.

A factor of fundamental importance in all of the preceding spot tests on reagent papers is the great reactivity of materials finely divided in the pores of the paper.   The effect of such great surface development is also well illustrated by an observation made by Pavelka[294] on the behavior of lead sulfate toward gallocyanine.   When precipitated in glass, $PbSO_4$ is only slightly tinted by this dye, whereas this salt is strongly colored when produced on paper by a spot reaction.   A delicate spot test for lead has been developed on the basis of this observation.

The number of cases in which a reaction can be analytically utilized only in the form of a spot test but not when carried out in a test tube is still small.   However, the mere existence of even these few cases is of fundamental importance.   On the other hand, it may be taken as a general rule that a reaction will have a greater sensitivity on a reagent paper than in a test tube.   The dimethylglyoxime test for nickel, and the Prussian blue test for ferrocyanide will serve to illustrate this point. As a test tube reaction, 2.8γ of nickel in 2 ml. of solution is revealed by the red dimethylglyoxime precipitate; this corresponds to the concentration limit $1:700,000$.   In contrast, if a drop (0.05 ml.) of a nickel solution is applied to dimethylglyoxime paper, a definite reaction is given by as little as 0.015γ of nickel ($1:3,300,000$).   Similar figures are obtained in the detection of ferrocyanide.   A positive result is just discernible if 3 ml. of a $1:400,000$ solution are treated with a ferric solution in a test tube, while on ferric chloride paper, a blue ring is produced by one drop of $K_4Fe(CN)_6$ solution, even at the dilution $1:700,000$.

Certain individual instances of the use of spot reactions on reagent papers have been known for a long time.[295]   A few years ago, Clarke and Hermance,[296] by means of comparative experiments, strikingly demonstrated the great improvement in sensitivity of spot tests that can be

[294] F. PAVELKA, *Mikrochemie* 7, 303 (1929).

[295] It is not certain who is to be credited with the first observation of an analytical use of spot reactions, and especially reactions on reagent papers.   The author believes that the first accurate description of a spot test was given by H. SCHIFF, *Ann.* 109, 67 (1859).   In this, a drop of urine was placed on paper impregnated with silver carbonate and a brown fleck of free silver was produced by the action of uric acid.   The credit seems to belong to Schiff all the more because by trials with dilute solutions of uric acid he expressly stressed the great sensitivity of this reaction.

[296] B. L. CLARKE and H. W. HERMANCE, *Ind. Eng. Chem., Anal. Ed.* 9, 292 (1937).

realized by the use of suitably prepared reagent papers. These studies will be referred to again in Chapter XI, where such reactions are discussed from the standpoint of their topochemical character. The discussion there will also include a consideration of protective layer effects, whose analytical significance and employment were established originally in connection with spot reactions conducted on paper.

In view of the great advantages that accrue from the use of reagent papers, it is fitting to insert here several salient features regarding their preparation. It would be most desirable if a very great variety of reagent papers were available for spot testing, but, for various reasons, this is not the case at present. Many reagent papers do not keep well, and must be prepared not too long in advance. Sometimes, considerable difficulties are encountered in securing uniform impregnation. Two methods of preparing reagent papers are used, depending on the nature of the impregnant. One procedure is to bathe filter paper in a solution of the particular reagent and then dry the paper. Even water-insoluble materials, can be incorporated in paper by this procedure if they will dissolve in low-boiling organic liquids. The other method, which applies exclusively to reagents that are not soluble in either water or organic solvents, consists in impregnating the paper with a salt solution and then bathing it in a solution of a suitable reagent so that precipitation occurs, so to speak, in the pores of the paper. Sometimes, a precipitation reaction can be followed by a second reaction that results in the desired reagent. In general, a much more uniform dispersion of materials in paper can be obtained by weak rather than by strong impregnation. This is in line with the fact, brought out in the discussion of spot pictures, that small quantities of colored precipitates may remain so finely divided in paper that they give the appearance of a fleck of a colored solution (see p. 576). However, strong impregnation is frequently desired; the danger then arises that the precipitate will not deposit uniformly. The impregnating material sometimes dusts off when the paper is dried, but more often this defect, which is due to a sort of aging, shows up when the prepared papers are stored. Although various materials display this undesirable characteristic to varying degrees, it also depends on the conditions prevailing during the precipitation, washing, and drying. The facts that various solids deposited in paper often behave quite differently with respect to the uniformity and permanence of their distribution, and that the precipitation conditions have a decided influence (Chapter XI), indicate that the form-species of the material to be incorporated in the paper and its adsorbability on the paper play a role. It is no accident that acid-base indicator papers have been known longer and are the most stable of all reagent papers. They are prepared by bathing filter paper in aqueous

or water-alcohol solutions of indicators or mixtures of indicators. These coloring matters are often colloidal or semi-colloidal in nature, and are irreversibly adsorbed on paper from their solutions. Consequently, there can be little doubt that the prevention of a rapid crystallization, and measures to keep the reagents contained in the paper within the colloidal range, are factors that make themselves definitely felt in the preparation of good reagent papers. Much work remains to be done along these lines.

The foregoing discussion of spot reactions on paper has been confined to instances that involve solutions of only a single material. Since the practical application of spot reactions usually requires that the simultaneous presence of several materials be taken into account, it would be of interest to examine the available knowledge concerning the possible alterations of spot pictures under such conditions. No systematic studies of this subject have appeared. The findings of Krulla (see p. 572) on adsorption in strips of filter paper, may be assumed to hold also in spot reactions, with respect to the width and displacement of adsorption zones. Considerable information is available regarding the lowering of the sensitivity of spot reactions by "indifferent" materials. No predictions can be made as to their effects, and the limiting proportions in each instance must be determined empirically. The analytically usable spot pictures that can be produced on reagent papers by systems containing several materials are of interest. The retention of the particles of the precipitate causes a precipitation and filtration to take place in the surface of the paper when precipitations are carried out as spot reactions (see p. 574). Consequently, it often is possible to detect, by a special test, the cosolutes that have migrated by capillarity into the zone that surrounds a spotted area. This zone corresponds, in a sense, to a filtrate, and it can be further extended, if need be, by applying a drop of water. Reagent papers that respond to only one ingredient of a solution are especially suitable for a procedure of this kind. For instance, if a drop of a solution containing ferric and aluminum salts is placed on a filter paper impregnated with potassium ferrocyanide, a central circle of Prussian blue is formed, surrounded by a moist zone in which small quantities of aluminum can still be detected by spotting with alizarin. The test for ferrocyanide and thiocyanate, by means of ferric chloride, is quite instructive. If ferric chloride is added to a test tube containing a solution of both ferrocyanide and thiocyanate, an excess of either of these ions makes it impossible to detect, without filtration, the one present in the lesser quantity. If, however, a drop of solution containing $Fe(CN)_6^{----}$ and CNS^- is brought onto filter paper impregnated with ferric chloride, then a central spot of Prussian blue appears surrounded

by a red border of ferric thiocyanate. According to Gutzeit,[297] even traces of ferrocyanide can be detected in the presence of a large amount of thiocyanate by this procedure.

The behavior of reagents that can react simultaneously with two or more materials to form precipitates is worthy of attention among spot reactions. The same precipitating agent can bring about a *fractional precipitation* from solutions, if the solubility products of the resulting precipitates are sufficiently different. However, a fractional precipitation of this kind can be successfully applied in a test tube only when the concentrations of the materials to be precipitated are not too different. Sometimes a particularly desirable analytical application may be made possible by carrying out fractional precipitations in the course of spot tests on reagent papers. For instance, rubeanic acid forms black, violet and brown precipitates respectively, with copper, nickel, and cobalt salts (see p. 249), and their simultaneous formation makes it difficult or impossible to detect these metals in a solution of mixtures of their salts. According to Feigl and Kapulitzas[298] a fractional precipitation and separation can be accomplished by using the following procedure. If a drop of a solution containing copper and cobalt is placed on a filter paper impregnated with rubeanic acid, a black or olive green ring, depending on the copper content, is formed in the middle of the test area, and around this is a concentric brown zone of cobalt rubeanate. For instance, 0.05γ Cu can thus be detected easily in the presence of 20,000 times this quantity of cobalt. The same identification limits and limiting proportions can be obtained by the fractional precipitation of copper and nickel rubeanate in separate zones. Small amounts of copper can also be detected in the presence of nickel and cobalt by fractional precipitation on rubeanic acid paper. Velculescu and Cornea[299] described another example of fractional precipitation on filter paper. They showed that concentric rings of the corresponding silver halides are formed if a drop of a solution containing iodide, bromide and chloride is placed on silver nitrate paper.[300] The fractional precipitation on reagent paper is therefore accompanied by a capillary separation of the precipitated products in distinct zones, which permits their recognition. Other tests based on such fractional precipitations followed by capillary separation are described in the author's Spot Tests.

This discussion of the use of characteristic spot pictures in qualitative

[297] G. Gutzeit, *Helv. Chim. Acta* **12**, 829 (1929); compare also F. Feigl, Spot Tests, p. 217.

[298] F. Feigl and H. J. Kapulitzas, *Mikrochemie* **8**, 239 (1930).

[299] A. Velculescu and J. Cornea, *Z. anal. Chem.* **94**, 225 (1933).

[300] F. Feigl, Spot Tests, p. 201.

analysis will be closed by a consideration of the interesting behavior of a $KMnO_4$-$K_2Cr_2O_7$ solution toward filter paper. It was observed[301] that when a drop of this mixture is placed on filter paper, the permanganate is rapidly reduced to MnO_2. The latter stays behind as a brown circle or ring, while the chromate travels outward and produces a yellow circular zone that is free of manganese. A closer investigation of this effect[302] revealed that it can be used to detect permanganate in the presence of chromate. In fact, this test is far superior to all of the earlier ones in certainty, speed, and sensitivity. As little as 0.3γ of $KMnO_4$ can be detected in one drop that also contains $20,000\gamma$ of K_2CrO_4, i.e., the saturation concentration of the latter salt. Interestingly enough, the stain produced by a dilute permanganate solution is decidedly weaker than the fleck that is formed when chromate is also present. The latter, *per se*, has practically no action on paper under the given conditions. This intensification probably can be explained as follows: The oxidative action on the cellulose by the permanganate forms products which, in contrast to cellulose itself, are oxidizable by chromate. Brown chromic chromate results and is precipitated concurrently with the brown manganese dioxide. Thus, the color strength of the fleck is heightened. Accordingly, this is an induced reaction, which can be seen readily, and is analytically useful only in the form of a spot test, but not when carried out as a test tube reaction. In those tests which succeed only as spot reactions on paper, the latter can be regarded as a *quasi* reactant. The partnership in the permanganate test in the presence of chromate is based on an actual chemical involvement of the cellulose of the paper.

Numerous illustrations have sufficed to demonstrate that the great surface development of finely divided materials may bring about analytically interesting effects in spot reactions on plain or reagent papers. However, it must not be forgotten that an extensive free surface can sometimes be a disadvantage. For example, materials finely dispersed in paper invariably react much more rapidly and to a greater extent than the compact materials when exposed to the air (autoxidation, action of carbonic acid, moisture, light). Such undesired changes must be given much closer attention when spot reactions are conducted on paper rather than in test tubes. For instance, very dilute alkali hydroxide gives an indistinct spot test on phenolphthalein paper; the red fleck disappears almost at once because the carbon dioxide of the air acts to form bicarbonate. If drops of solutions of alkali sulfides, stannites, or ferrocyanides are placed on filter paper, autoxidation proceeds, both during and after

[301] F. FEIGL, Spot Tests, p. 261; Laboratory Manual, p. 84.
[302] F. FEIGL and H. A. SUTER, *Chemist-Analyst* **32**, 4 (1943).

the evaporation of the water, at a much higher rate than when these materials are in compact form or in solution.

The high degree of dispersion along with autoxidation can be held responsible for the fact that lead sulfide, if finely distributed in filter paper, is dissolved even by hydrochloric acid that is so dilute that it is without any discernible action on compact sulfide. The effect is easily seen if a very dilute lead salt solution is used to prepare the PbS paper.[303] If a drop of a solution of Schlippe's salt (Na_3SbS_4) is applied to filter paper, a uniform and increasingly greater separation of Sb_2S_5 (probably plus some oxysulfide) occurs within a few minutes. This is due to autoxidation, despite the fact that Schlippe's salt, in crystals or in solution, is stable to air.

It should also be noted that filter paper, aside from its unavoidable content of tiny quantities of mineral matter,[304] is by no means a completely indifferent material. Practical use was made of its activity in the test for permanganate just described. Consequently, filter paper, which is a very surface-rich system of cellulose capillaries closely knit together, may enter into redox reactions after more or less prolonged contact with reducible materials. Excellent examples are its marked reduction of ferric salts and alkali ferricyanides. Likewise, many organic nitro compounds, e.g., dipicrylamine, are reduced by filter paper. Sometimes (see Chapter IV) materials adsorbed on filter paper lose their normal reactivity wholly or in part. In such cases, the paper acts as a *quasi* masking agent.

The foregoing discussion shows that spot pictures are produced not only by the particular chemical reaction, but that capillary spreading, diffusion, adsorption, and the fine dispersion of materials, also invariably play a role. Hence, the seemingly simple procedure of making a spot test on filter paper in reality consists of a number of concurrent and successive partial processes, and the final aspect of a spot picture is determined by the sum total of the effects of these individual processes. Despite this complexity, spot pictures that are formed under comparable conditions are strictly reproducible. This is especially true if dilute solutions are employed and, for the most part, only such are used in practice. In general, the cosolutes in dilute solutions seem to give little trouble with respect to any significant alteration of the spot picture. This is especially important in spot colorimetry. The underlying principle of this micro method of quantitative determination is a com-

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[303] H. E. FEIGL, unpublished studies.

[304] H. RANKAMA, *Bull. comp. geol. Finlande* **126**, 14 (1939) found that paper ash, besides SiO_2, contains numerous metal oxides combined with silica. For instance, he reports that 0.1% PbO, 0.3% ZnO, and 0.3% SnO_2 are present.

parison of color intensities.   A series of standard solutions of the material to be determined is prepared, i.e., a number of solutions containing known concentrations of the pure material.   An appropriate color reaction is carried out with single drops of these solutions on a spot plate or filter paper, and a series of colored drops or flecks of graded intensity results.   The same color reaction under as identical conditions as possible, is then conducted with a drop of the test solution, and the intensity is compared with the color scale prepared from standard solutions.[304a] The procedure is sufficiently accurate, at least for orientation purposes. to indicate with which standard fleck there is agreement in color intensity. Hence, conclusions can be drawn about the quantity of the particular material present.   Spot colorimetric determinations by means of color comparisons are most exact when carried out on spot plates if soluble colored compounds are involved, because turbidities render a color comparison difficult.   On the other hand, even small amounts of colored insoluble materials can be satisfactorily compared on paper, because, as has been shown, the fine distribution of small amounts of a precipitate throughout the pores of the paper produces a kind of homogenization (see p. 576).   It was pointed out in the discussion of the morphology of spot pictures that flecks formed by the deposition of insoluble colored reaction products are often not uniform throughout their entire extent but, because of adsorption and diffusion, ring zones of various color intensities can also result.   Obviously, this condition can seriously reduce the nicety of a comparison of colored flecks.   Yagoda[305] eliminated such interferences to a considerable degree, when he introduced "confined spot test papers," a most ingenious device.   They are squares of filter paper, carrying rings of water-repellant or water-insoluble materials that form the boundaries of circular reaction fields, whose areas range from 10 mm.[2] upward.   When a drop of a solution is placed on an enclosed reaction paper of this kind, there can be no lateral capillary spreading beyond the barrier ring.   The main portion of the liquid, along with the material dissolved in it, at first remains as a globule on the paper.   It then is forced to pass into the interior of the paper, especially if gentle suction is applied to speed up this penetration.   Thus, if the paper is impregnated with suitable reagents, the reaction occurs within a limited space and the result is the continuous deposition of colored reaction products and the development of a uniformly colored fleck.   The latter is precisely what is needed for a satisfactory color comparison.   The use of confined spot test papers obviously need not be limited to single

[304a] N. A. TANANAEFF, made the first observations on spot colorimetry in 1928.

[305] H. YAGODA, Ind. Eng. Chem., Anal. Ed. 9, 79 (1937); Mikrochemie 24, 117 (1938).

drops. Several drops may be applied, or if larger reaction fields are employed, known volumes of a test solution can be subjected to passage, with concurrent reaction, through suitable reagent papers. The accuracy of spot colorimetric determinations is thus increased, and furthermore the limits of the quantities of the material that can be determined by colorimetric comparison are extended. Spot colorimetry has been used almost exclusively in inorganic analysis.[306] There is little doubt, however, that it will eventually be adapted also to organic analysis, and that the Yagoda procedure especially will be applied in a variety of ways.

Chromatography

The foregoing discussion has repeatedly indicated the great advantage contributed to spot testing by the capillary and adsorptive phenomena associated with reactions carried out on filter paper, and likewise the usefulness of the marked reactivity of finely divided materials. However, it must be remembered that, although capillarity and adsorption are utilized often in increasing the selectivity of spot tests, they usually are no more than aids in securing this objective. Many drop tests are not necessarily conducted on paper; in fact, certain reaction requirements definitely ban the use of paper. On the other hand, chromatographic analysis, like the Goppelsroeder capillary analysis, is based entirely on the use of adsorption to separate materials. Schönbein and Goppelsroeder's investigations of the capillary and adsorption phenomena that are exhibited so characteristically when dye solutions ascend filter paper, were probably known to Goppelsroeder's contemporary, M. Tswett, a Russian botanist. Possibly, their work led him to make the experiments, which later acquired a singular importance. He allowed a petroleum ether extract of leaves to flow through a vertical tube charged with finely divided calcium carbonate. The packing was then washed with fresh solvent and colored rings or bands appeared. These were separated mechanically and then shaken individually with methyl alcohol, which extracted the adsorbed pigment. By the aid of this procedure, Tswett became the first to show that the green pigment of leaves contains four main components, which are now called chlorophyll a and b, xanthophyll, and carotene. He named the procedure chromatographic analysis. Although Tswett published a number of papers on his new technic, it attracted no particular attention. For more than a century, crystalline carotene had been supposed to be a homogeneous substance. Twenty-five years after the publication of Tswett's first

[306] A rather detailed description of spot colorimetric determinations is given in Chapter IX of F. Feigl's Laboratory Manual.

paper in German,[307] Kuhn and Lederer[308] resolved carotene into two isomeric hydrocarbons, α- and β-carotene, by adsorption on columns of fibrous alumina. Shortly thereafter, Kuhn, Winterstein and Lederer[309] extended the use of column adsorption to prepare crystalline leaf xanthophyll (lutein) and to isolate the xanthophylls of egg yolk. Following upon this reintroduction, Tswett's method was successfully employed by many workers, especially for the preparative separation of organic compounds. This procedure of chromatographic adsorption analysis, which is now commonly called chromatography, not only rightly deserves a place by the side of the two classical methods of accomplishing such separations, but in fact it often is superior to crystallization and distillation. One of the special merits of column adsorption is that it can be used successfully to isolate quantities of a material that are so small that they cannot be handled by other methods of separation. Another important feature is that it spares the material from deleterious treatments, because it can be carried on without raising the temperature and, when necessary, with exclusion of air. As a consequence, this technic has grown far beyond the analytical uses foreseen by its inventor. Numerous important advances in the elucidation of the composition of natural products could not have been achieved without the use of chromatography. In the biological sciences certain insights into the physiological activity of small amounts of various material were gained solely because this method was available. Furthermore, the boundaries between a preparative and an analytical utilization of chromatography approach each other quite closely; they practically disappear when small quantities of materials are being quantitatively isolated and separated.[310] It is beyond the scope of this book to go into the technical details of chromatographic procedures or to discuss concrete examples of their application. This is all the less necessary because so much information and data have been amassed in a short period that excellent books on this subject are now available.[311] Consequently, the following discussion

[307] M. TSWETT, *Ber. deut. botan. Ges.* **24**, 234, 316, 384 (1906).
[308] R. KUHN and E. LEDERER, *Ber.* **64**, 1349 (1931).
[309] R. KUHN, A. WINTERSTEIN and E. LEDERER, *Z. physiol. Chem.* **197**, 141 (1931).
[310] Analogous considerations hold also for the application of chemical reactions. Many methods of detection and determination are nothing but preparative procedures that give 100% yields when carried out with small quantities. The common differentiation between analysis and synthesis in the sense of a tearing down or building up of materials is really not valid. Most cases of analytical reactions involve mutual substitutions, many in fact are true synthetic reactions. Only in a relatively few instances (*e.g.*, reductions) are true degradation reactions employed.
[311] L. ZECHMEISTER and L. v. CHOLNOKY, Principles and Practice of Chromatography (translated by A. L. Bacharach and F. A. Robinson), New York, 1943; H. H.

will be confined largely to those facts concerning chromatography that are of significance for the attainment of specific and selective adsorption separations.

Tswett's original experiment exhibits the basic idea of chromatography. If a solution is sucked or forced through a vertical column composed of a suitable adsorbent, the various solutes will be fixed in different sections of the column according to their respective adsorbabilities. This separation becomes still more effective if finally the pure solvent is drawn through the adsorbing system. The following terms are commonly employed. (a) The series of adsorption zones is called a chromatogram. (b) The percolation of fresh solvent through the column, which often results in a better separation of the adsorption zones, is known as the development of the chromatogram. (c) The extraction of the adsorbed materials from the adsorption column is called elution, and the solvent used for this purpose is called the elution medium, or eluant (eluent).

The separate adsorption zones are directly apparent to the observer when colored materials have been subjected to the Tswett procedure. The term chromatogram[312] is particularly apt for an adsorption picture of this kind. However, the principle of adsorptive separation in columns can also be applied to mixtures of colorless compounds, and the designation is not fitting in such cases. Nevertheless, certain workers speak of a colorless chromatogram, which obviously is a contradiction of terms. Sometimes an invisible chromatogram becomes apparent if it is observed in ultraviolet light. This expedient was originated by Winterstein[313] and independently by Karrer.[314] The latter suggested that the procedure be called ultrachromatography.

The various materials contained in a chromatogram are always associated with the solvent and the adsorbent. Therefore, the local accumulation of a material by column adsorption is a step preliminary to the actual isolation of the material and to the making of analytical tests. The process of elution, which is a desorption, leads to solutions from which the previously adsorbed materials can be isolated in a pure condition by crystallization, *etc.* An identification can be made in the eluent (after concentration when necessary) by chemical reactions, by taking

STRAIN, Chromatographic Adsorption Analysis, New York, 1942; H. WILLSTAEDT, L'Analyse chromatographique et ses applications, Paris, 1938; T. I. WILLIAMS, An Introduction to Chromatography, London, 1946; H. G. Cassidy and others, Chromatography, New York, 1948; A. P. Martin, *Endeavour* **6**, 21 (1947).

[312] From the Greek *chroma* = color and *gramma* = writing.

[313] A. WINTERSTEIN, *Z. physiol. Chem.* **230**, 139 (1934).

[314] P. KARRER, *Helv. Chim. Acta* **17**, 693 (1930).

the melting point, by physiological tests, *etc.* The materials localized in the bands of a chromatogram can sometimes be separated from the adsorbent by dissolving the latter in water or in chemically active agents, which leave the adsorbed material unchanged. When invisible chromatograms are obtained, the column can be segmented and the parts then eluted individually. Testing of the separate eluates will then disclose the location of the adsorption bands in the column. Zechmeister[315] was the first to use successfully a procedure that has great importance for analytical purposes. It consists in brushing the adsorption column with suitable color reagents that respond to the materials localized in the chromatogram. This method can be used, for instance, to detect aldehydes with fuchsin-sulfurous acid, unsaturated compounds with permanganate, and amines with diazotized sulfanilic acid. This procedure is a combination of chromatography and spot test analysis; it presents a broad field for the application of sensitive reactions. In some cases, it has been found feasible to treat a mixture of materials initially with a color reagent and then, by means of a chromatogram, to separate the resulting soluble reaction products, which could not be distinguished from one another when in solution together.

The preceding preliminary, and consequently incomplete, remarks may have given the impression that the separation of materials by the chromatographic procedure is enticingly simple. This simplicity actually exists, once the chromatogram is formed. The difficulty of the method lies in the production of a good chromatogram. There are, as yet, few guiding principles for making accurate predictions as to when and under what conditions chromatograms will be obtained that can be utilized for preparative and analytical purposes. Unknown systems of organic compounds must be treated empirically, or the experience gained in analogous cases can be called on. This condition is understandable if it is recalled that the essence of chromatography is adsorption from a solution, and the latter in turn depends on the nature of the dissolved material, the solvent, and the adsorbent. Consequently, for a given substance, the adsorbent and the solvent form the adsorption *milieu*, which determines the success of a chromatographic separation. Obviously, there is ample possibility for great variability in adsorption even when the same solvent is used and only the adsorbent is varied. The possibility of variation becomes still greater if a different solvent is also used, and likewise if solutions containing more than a single solute are involved. The dominant role of a solvent lies in the fact that it, as well as the solute, is retained on the adsorbent. The more strongly a solvent is adsorbed, the more vigorously does it compete with the dis-

[315] L. Zechmeister, *Bull. soc. chim. biol.* 18, 1885 (1936).

solved material for the adsorbent (or its active areas). Since, on the other hand, the adsorbents employed in chromatography vary between wide limits in their capacities to adsorb solvents and dissolved materials, the strength of the adsorption can often be regulated to an extraordinary nicety by a suitable combination of adsorbent and solvent. Thus they can be adapted to provide the conditions at which an optional separation can be expected. Such combinations, which frequently must be discovered by trial, are particularly possible in the separation of organic compounds, for which there is usually a wide choice of solvents or solvent mixtures. This is the chief reason why chromatographic separations have become so important in the organic field.

If adsorption is considered as a binding of the adsorbed material to the adsorbent, then the removal from its solution of a dissolved material by adsorption is a kind of precipitation. Hence, a chromatogram presents, to a certain extent, the picture of a fractional precipitation on the adsorption column, and it is occasioned by the differing strengths of the adsorption affinities. Materials, which are very similar in other respects, often diverge markedly with respect to their adsorbability, and therefore as to the location of their adsorption zones in the column. This fact is the result of the action of adsorption affinities of different intensities. Consequently, an adsorption can bring to light differences in affinity which cannot be detected by chemical reactions, and thus it becomes possible to develop specific and selective adsorptive separations of materials which cannot be distinguished from each other by purely chemical methods. Slight differences in adsorption. affinity become particularly significant in the development of the chromotogram, which is the most important step in many chromatographic processes. This development consists of a continuous desorption and readsorption of dissolved particles, which are thus given an opportunity to become fixed in sharply separated zones of the adsorption column. Both the development and the elution are reversible adsorption processes or, more correctly, displacements of feebly adsorbed materials from the column by adsorption of the solvent, which is present in large excess, in their stead. Accordingly, reversible loose adsorption, which usually has little significance in analytical procedures, plays a dominant role in chromatography. This statement should not be taken as an implication that chromatography involves reversible adsorptions exclusively. In truth, all types of adsorption are possible here, including irreversible adsorption. The occurrence of the latter is revealed by the fact that the position of an adsorption band in the column is not changed when the chromatogram is developed. Negative adsorption occurs also in chromatography, as well as in capillary analysis and spot testing. If an adsorption band is

formed in an adsorption column only beneath a zone occupied by the solvent, then the space traversed to reach the site of the formation is nothing other than the zone of negative adsorption. Consequently, the entire process of an adsorption from a solution is divided by chromatography into its partial processes: adsorption of solvent; positive and negative adsorption of dissolved materials; fractional adsorption of dissolved materials. Fundamentally, every employment of chromatography for preparative and analytical purposes rests on this fact.

TABLE XXVI

Various Substances and the Adsorbents and Solvents Used in Their Preparation and Purification by Chromatographic Methods

Substance	Adsorbent	Solvent
Enzymes..............	Bauxite	Water
Sugar................	Bauxite	Water
	Bone ash	Water
Flavins.......	Frankonite	Water
Anthocyanins..........	Alumina	Water
Alkaloids.............	Alumina	Benzene or water
Amino acids...........	Titania	Water
Chlorophylls......... .	Saccharides	Petroleum ether and benzene
	Magnesium citrate	Ether and petroleum ether
Chlorophyll derivates..	Talc or saccharides	Benzene, ether or alcohols
Nitro compounds.......	Talc or alumina	Benzene
Organic acids..........	Talc	Benzene
Phenols...............	Lime	Alcohols
	Alumina	Benzene
Ethers, ketones and esters..............	Alumina	Petroleum ether and benzene
Xanthophylls..........	Alumina	Benzene
	Magnesia	1,2-Dichloroethane
	Alkaline earth carbonates	Petroleum ether or benzene or carbon bisulfide
Aliphatic alcohols and sterols.............	Alumina	Petroleum ether and benzene
Unsaturated hydrocarbons.	Lime, alumina or magnesia	Petroleum ether, carbon tetrachloride or benzene
Saturated hydrocarbons.	Alumina or magnesia	Petroleum ether

Table XXVI gives a brief summary of chromatographic methods for the purification and isolation of organic compounds of the most varied types. It also shows the wide variety of adsorbents and solvents that can be used in chromatographic separations.

Examination of this Table will show that the adsorbents used in

chromatography are, without exception, oxygen-containing inorganic and organic compounds. Such materials have a great capacity for adsorbing water, and show little tendency to adsorb nonpolar organic liquids. Accordingly, they are called hydrophilic adsorbents. Hence, they extract from aqueous solutions only those materials that are more strongly adsorbed than water. As a rule, they have considerable ability to adsorb polar organic compounds from solutions in slightly polar or nonpolar liquids. Hence, organic liquids find frequent use as solvents in chromatography. The marked adsorbability of water (and the water-similar lower alcohols) is the reason these liquids act and can be used as eluants, *i.e.*, they dispossess the adsorbed material. Hydrophilic adsorbents are not alike in their activity, and even uniform fine pulverization does not make them so. Although the increased surface resulting from finer grinding can raise the adsorption ability of a given adsorbent, the character and quality of the adsorption cannot be changed by pulverization. Consequently, hydrophilic adsorbents are only similar in their behavior, and only in the sense that they fix various materials in the same order, but with varying degrees of tenacity. A number of hydrophilic adsorbents are given, in the order of increasing adsorption capacity in Table XXVII. This arrangement, however, provides only a preliminary orientation. The history of the adsorbent, *i.e.*, the method by which it was prepared, often has a decided effect, and suitable measures may often accomplish either an activation or deactivation of a particular adsorbent. A partial deactivation is often desired for practical reasons, because firmly adsorbed materials do not permit a satisfactory development of a chromatogram, *i.e.*, the adsorption zones cannot be resolved. Furthermore, partial deactivation is often advantageous if strong adsorption leads to undesirable changes, such as autoxidation, rearrangement, *etc.* Ordinarily, adsorbents can be deactivated by treatment with water or alcohol, followed by drying at room temperature. Such treatment obviously results in the fixation of water or alcohol, and the adsorption capacity of the adsorbent is thereby decreased.

The choice of suitable solvents is determined first of all by the solubility of the material to be adsorbed. It also depends, of course, on the solubility of the adsorbent. Hydrophilic adsorbents show the greatest adsorption ability for materials dissolved in' saturated hydrocarbons. They adsorb more poorly from solutions in unsaturated and cyclic hydrocarbons, chlorinated hydrocarbons, ketones, or esters, and still less from solutions in alcohols, nitrogen bases, and water. A general, though not invariable rule is: solvents from which the adsorption is weak, are good eluants. Furthermore, liquids that are more polar than an adsorbed material can displace the latter from the adsorbent. A number of liquids,

that are used as solvents or in solvent mixtures for materials destined to
be adsorbed, or as elution media, are given in Table XXVII.

TABLE XXVII

Adsorbents and Liquids Arranged in Approximate Order of Their Influence on Adsorption

Hydrophilic Adsorbents[a]	Liquids[b]
Sucrose, starch	Petroleum ether, b.p. 30–50°C.
Inulin	Petroleum ether, b.p. 50–70°C.
Magnesium citrate	Petroleum ether, b.p. 70–100°C.
Talc	Carbon tetrachloride
Sodium carbonate	Cyclohexane
Potassium carbonate	Carbon bisulfide
Calcium carbonate	Ether (anhydrous, alcohol-free)
Calcium sulfate	Acetone (anhydrous, alcohol-free)
Calcium phosphate	Benzene (toluene)
Magnesium carbonate	Esters of organic acids
Magnesia	Chloroform (1,2-dichloroethane, dichloromethane)
Lime (freshly and partially slaked)	Alcohols (*n*-propyl, butyl)
Activated silicic acid	Water (variations with changes in pH and salt concentration)
Activated Mg silicates	Pyridine
Activated alumina and magnesia	Organic acids
Fuller's earths	Mixtures of acids or bases with water, alcohol or pyridine

[a] Arranged in the order of increasing adsorption capacity.

[b] Arranged in the order of increasing self-adsorption, decreasing adsorption of
materials dissolved in them, and increasing eluting action.

It has already been pointed out that the adsorption medium and the
solvent constitute the adsorption *milieu*, which determines the tenacity
of an adsorption and the adsorptive separations of materials.   It may be
deduced, from information such as is contained in Table XXVII, that
in chromatography the same *milieu* may be set up in various ways.   For
instance, a strong adsorbent may be combined with a fairly adsorbable
solvent (*e.g.*, Al_2O_3 + ether), or a weak adsorption medium can be used in
conjunction with a solvent whose adsorption is especially weak (*e.g.*,
$CaCO_3$ + petroleum ether).   Numerous possibilities of such variation
exist.

The selectivity of chromatographic separations can be utilized for
analytical purposes in two ways: (a) in indirect form, as a method for the
local accumulation of a material preliminary to identity tests or quanti-
tative determinations; (b) in direct form, by comparing the location of
adsorption zones in the column.   This latter method is particularly
valuable in testing materials.   For example, the homogeneity of a mate-
rial can be investigated chromatographically, since the requirement in
this case is the production of only one adsorption zone in the column.

The identity of substances can be assumed, if a solution containing all of them produces a mixed chromatogram in a single zone. This procedure is analogous to the taking of mixed melting points. Complex products, such as foods and condiments, oils, tanning agents, dyes, drugs, soil extracts, *etc.*, can often be distinguished by the definite and characteristic chromatograms produced by the materials themselves or their extracts. Likewise, adulterations and artificial coloring of products can be revealed by abnormal chromatograms. All of these applications involve an extension and refinement of the Goppelsroeder capillary analysis, to which, in fact, chromatography is closely related.

It was pointed out on p. 593 that the adsorption of materials in different zones of an adsorption column can be ascribed to the action of weak binding forces, which cannot be detected by chemically active agents or through the realization of reactions that can be formulated stoichiometrically. Lacking a more concrete characterization, these forces have been quite generally termed adsorption affinities. Unquestionably, there are relations between such adsorption affinities and the structure of an organic molecule or of the atomic groupings or linkages contained in it.[315a] All experience demonstrates that the adsorbability of organic compounds is influenced to a marked extent by the nature and number of polar groups in the molecule. The following arrangement shows this:
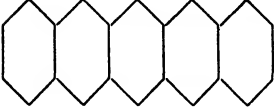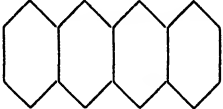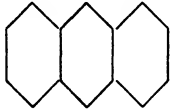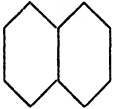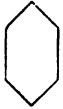
Acids and bases	Most strongly adsorbed
Hydroxy, amino, thio, nitro compounds	
Aldehydes, ketones, esters	
Halogen compounds	
Unsaturated hydrocarbons	
Saturated hydrocarbons	Most weakly adsorbed

In actual practice it is not possible to separate by chromatographic methods all types of organic compounds on the basis of their content of polar groups. Other factors also play a role. The size and the weight of the organic molecule are a prime consideration; in general, larger and heavier molecules are adsorbed better (see later). Furthermore, the polarity of a group is affected by its position in the molecule, and by other groups in the molecule. The more complex the framework of a molecule, the more difficult it is to draw conclusions as to constitutional influences from the position of an adsorption zone in the column. However, definite relationships between constitution and absorbability can often be established for organic compounds of a given class. Since mixtures of similar materials are often encountered in practice, chromatographic

[315a] L. ZECHMEISTER, *Am. Scientist* **36**, 505 (1948) suggested the appropriate term "anchoring groups" for such atomic groups as have a decisive function in chromatographic adsorption.

adsorption provides a particularly valuable aid in the solution of this type of difficult problem in organic analysis. Systematic studies of constitutional influences on chromatographic separations of organic compounds were first made by Winterstein; his lead was followed by others. Only a few characteristic examples will be cited from among the numerous investigations along this line.[316]

Winterstein and Schön[317] discovered a regularity in the column adsorption of the following series of aromatic hydrocarbons:

	2,3,6,7-dibenzanthracene	$C_{22}H_{14}$	Most strongly adsorbed
	Naphthacene	$C_{18}H_{12}$	
	Anthracene	$C_{14}H_{10}$	
	Naphthalene	$C_{10}H_8$	
	Benzene	C_6H_6	Most weakly adsorbed

It is evident from this series that an increase in adsorbability occurs with rise in molecular volume and molecular weight. The same effect was found by these workers in a series of diphenylpolyenes, which consequently are easily separated from each other by the chromatographic method:

C_6H_5—CH=CH—CH=CH—CH=CH—CH=CH—C_6H_5 Most strongly adsorbed
(diphenyl octatetraene)
C_6H_5—CH=CH—CH=CH—CH=CH—C_6H_5
(diphenyl hexatriene)
C_6H_5—CH=CH—CH=CH—C_6H_5
(diphenyl butadiene)
C_6H_5—CH=CH—C_6H_5
(stilbene)
C_6H_5—C_6H_5
(diphenyl)   Most weakly adsorbed

[316] For an extended treatment see L. ZECHMEISTER and L. v. CHOLNOKY, *op. cit.*
[317] A. WINTERSTEIN and K. SCHÖN, *Z. physiol. Chem.* **230,** 146 (1934).

Here the distinct effect exerted on the adsorbability by the presence of even one extra double bond is especially interesting. In addition, the higher members of the series are more intensely colored than those below them, and accordingly there is also a relationship between the adsorbability and color.

Ruggli and Jensen[318] have demonstrated the decided effect of double bonds in the column adsorption of several dyes of the indolenin series:

$$
\begin{array}{cc}
\text{CH}_3 & \text{CH}_3 \\
|\!-\!\text{CH}_3 \quad \text{H}_3\text{C}\!-\!| \\
\text{C} \\
\text{N} \qquad \text{H} \qquad \text{N} \\
\text{CH}_3 \qquad \text{H}_3\text{C} \quad \text{Cl}
\end{array}
$$

indolenin yellow weakest adsorption

R = CH—CH=CH—R′   indolenin red

R = CH—CH=CH=CH—R′   indolenin violet

R = CH—CH=CH—CH=CH—CH=CH—R′ indolenin blue   strongest adsorption
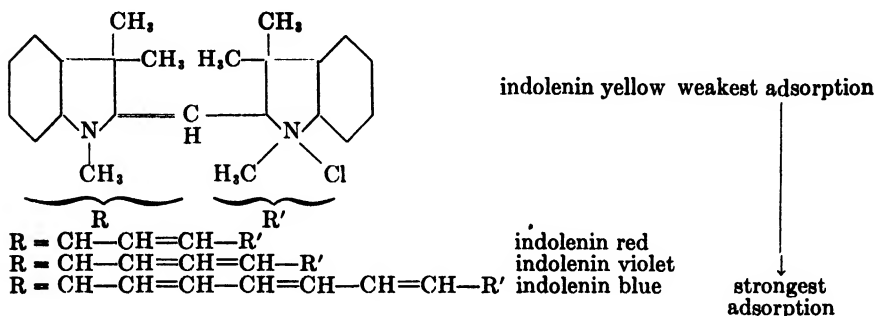
In this series, there is not only an increase in the number of double bonds, but the molecular weight rises, and the color deepens. Ruggli and Jensen (*loc. cit.*), by their study on the chromatographic separability of various halogen derivatives of fluorescein have shown the manner in which deepening of color and increase of the molecular weight alone affect the position of adsorption zones:

Dye	Molecular weight	Color	
Rose bengale (4I, 2Cl)..............	905	Blue-red	strongest adsorption
Erythrosin (4I)........	836	Bluish-red	
Eosin (4Br)......................	648	Red	
Fluorescein (no halogen)............	332	Yellow	weakest adsorption

The following findings indicate the effectiveness of chromatographic separations in establishing even slight differences in the constitution of isomeric compounds. Karrer and Nielsen[319] showed that, among the three isomeric mononitrophenols and mononitranilines, the adsorbability on an Al$_2$O$_3$ column decreases from the *para*, through the *meta*, to the *ortho* compound. Consequently, it is possible to separate these isomers chromatographically. The sodium salt of 2-naphthol-4-sulfonic acid

[318] P. Ruggli and P. Jensen, *Helv. Chim. Acta* 18, 624 (1935); 19, 64 (1936).

[319] P. Karrer and N. Nielsen, Zanger Festschrift, p. 954. Zurich, 1934.

(I) is more strongly adsorbed than the isomeric salt of 1-naphthol-4-sulfonic acid (II).   Likewise, naphthacene (III) is more adsorbable than its isomer chrysene (IV):
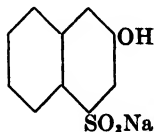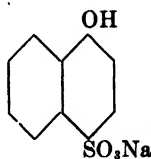
(I)   (II)
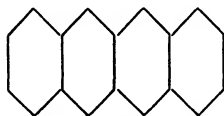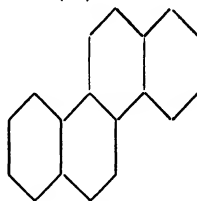
(III)   (IV)

The foregoing examples should suffice to demonstrate that the selectivity of the Tswett adsorptive separation often is truly astounding, and also to illustrate the influence of constitutional factors on the adsorption of organic compounds.   Studies of the relationships between group action and adsorbability have about the same significance for chromatographic adsorption analysis as investigations of the relations between atomic grouping and selective action in precipitation and color reactions by means of organic reagents (compare Chapter VI).   Every advance toward a better understanding of such relationships is of great value in the attempt to achieve selective, specific, and sensitive methods of detection, determination, and separation.[320]

Chromatography is used principally in the separation of organic, mostly non-dissociating, compounds, but is not limited to these.   Since 1937, Schwab and his associates[321] have shown, in numerous studies, that inorganic, dissociable salts, or their ions, can also be fixed in an adsorp-

[320] The value of the experimental studies along this line should be neither over- nor underestimated.   The results of such investigations will not make it possible to discover new tests or suitable adsorptive separation methods right off.   However, certain guiding principles for such researches will be obtained, and various possibilities can be compared with a fair degree of their probable success.   In addition, the assembling of experimental findings yields statistical material, which, at a later period, can form the basis for the development and testing of more general regularities and rules.

[321] G. M. Schwab, Z. Elektrochem. 43, 791 (1937); G. M. Schwab and K. Jockers, Z. angew. Chem. 50, 546 (1937); G. M. Schwab and G. Dattler, ibid. 50, 691 (1937); 51, 709 (1938); G. M. Schwab and A. N. Ghosh, ibid. 52, 666 (1939); 53, 39 (1940).

tion column.[322] The available data indicate that inorganic chromatography involves exchange adsorption exclusively, in contrast to organic chromatography, in which addition adsorption predominates. The technic is the same in both cases, but the only suitable adsorption media for inorganic ions are those which contain exchangeable ions with charges of the same sign. Cation adsorption is best carried out on Al_2O_3 that contains some free alkali and reacts strongly basic in aqueous suspension.[323] Alumina that has been pretreated with mineral acids is suitable for the exchange adsorption of anions. If a salt solution which contains a cation that can be exchanged for alkali ions is passed through the basic Al_2O_3, the cation stays in a definite zone of the adsorption column and displaces alkali ions. Metal ions that have been retained can be displaced again if the solution contains ions which are fixed more tenaciously, or whose hydroxides are less soluble. The dispossessed ion travels onward in the column until it again reaches unoccupied spots of the adsorption medium, where it is retained. Zones formed in this manner, in contrast to adsorption zones of organic compounds, conform to the following rules: (a) the zones adjoin each other directly; (b) the finished developed zones are not moved forward nor do they spread when water is passed through the column; (c) the width of the zones is proportional to the quantity of adsorbed material.

The adsorption band produced by a cation on a basic alumina column has the color of the respective hydroxide or basic salt. In fact, these compounds are formed, and the color is not that of the aluminate, as

[322] The first record of the fixing of inorganic compounds in definite zones of an adsorption column is that of L. REED [*J. Chem. Soc., Abstr. Proc.* **VIII-IX**, 123 (1892-93)]. He showed that if a solution of potassium chromate and potassium eosinate, or of ferric chloride and copper sulfate, passes through a narrow tube filled with kaolin, the dissolved materials are retained in different zones. He was not only responsible for the first attempt of an inorganic chromatography, but he preceded M. Tswett, though without success, in attempts to separate organic compounds (especially alkaloids) by column adsorption. His observations appear to have been overlooked, perhaps because they were included in a paper that dealt primarily with the capillary spreading of salt solutions in paper (compare p. 571).

[323] The exchange ability of the alkali is not influenced by whether the free alkali is adsorbed on Al_2O_3 as hydroxide, carbonate or bicarbonate, or whether it is present as an aluminate. The presence of alkali is important because washed Al_2O_3 that is perfectly free of alkali is not suitable for inorganic cation chromatography, nor for the adsorption of organic cations, for instance, from solutions of alkaloid salts. [Compare, in this connection G. SIEWERT and H. JUNGNICKEL, *Ber.* **76**, 310 (1943).] Conversely, such Al_2O_3 is just as good as Al_2O_3 containing alkali for the chromatography of organic compounds that are nonelectrolytic in character. The differences between addition and exchange adsorption, which both play a role in chromatography, are plainly exhibited here.

has been mistakenly assumed by some workers.   Studies of the separation of binary mixtures have revealed the following sequence in the retention of the most important cations on Al_2O_3:

$$
\begin{array}{lll}
H^+ & \rightarrow Cr^{+++},\ Fe^{+++},\ Hg^{++} & \rightarrow Zn^{++} \\
\downarrow & \downarrow & \downarrow \\
As^{+++} & UO_2^{++} & Fe^{++},\ Cd^{++},\ Co^{++},\ Ni^{++} \\
\downarrow & \downarrow & \downarrow \\
Sb^{+++} & Pb^{++} & Tl^+ \\
\downarrow & \downarrow & \downarrow \\
Bi^{+++} & Cu^{++} & Mn^{++} \\
& \downarrow & \\
& Ag^+ &
\end{array}
$$
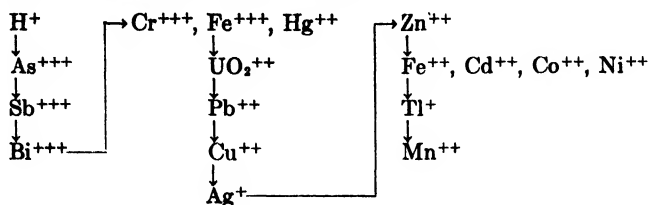
(The cations on the same line produce mixed and not individual zones, *i.e.*, they are held with equal intensity.)

Since only certain metal hydroxides or basic salts are colored, it usually is necessary to employ special means to render the zones visible. Hence, a suitable reagent solution (alkali sulfide, ferrocyanide, *etc.*) is passed through the column[324] to develop colored bands of the respective sulfides, *etc.*   Schwab showed that a number of tests for the ingredients of mixtures can be made successfully in this manner.   He and his coworkers made the interesting discovery that the relative position of metals in adsorption zones of an Al_2O_3 column is changed from that just given if the metals are present as complex rather than simple ions.   For instance, sequence (I) is obtained with an ammoniacal solution of ammine-forming metals; sequence (II) results when a basic tartrated solution is passed through the column:

$$
Co \rightarrow Zn \rightarrow \begin{pmatrix} Cd \\ Cu \end{pmatrix} \rightarrow Ni \rightarrow Ag \qquad\qquad Pb \rightarrow Cu \rightarrow Bi \rightarrow Fe^{III} \rightarrow Cr
$$

$$
\text{(I)} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(II)}
$$
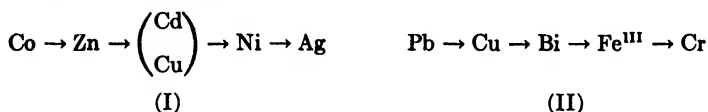
Schwab made analytical use of this shift of position of metals in the adsorption column after producing complexes with ammonia or tartrate.

It has been pointed out (see p. 601) that the chromatographic retention of anions requires the use of an acidified alumina, *i.e.*, an Al_2O_3 on which acids (anions) are adsorbed.   This material allows cations to pass freely, just as basic Al_2O_3 offers no hindrance to the passage of anions. The anions are retained in the following characteristic order:

$$
\begin{array}{lll}
OH^- & \rightarrow SO_4^{--} & \rightarrow MnO_4^- \\
\downarrow & \downarrow & \downarrow \\
PO_4^{---} & Fe(CN)_6^{---},\ Cr_2O_7^{--} & ClO_4^- \\
\downarrow & \downarrow & \downarrow \\
F^- & Cl^- & S^{--} \\
\downarrow & \downarrow & \\
Fe(CN)_6^{----},\ CrO_4^{--} & NO_3^- &
\end{array}
$$
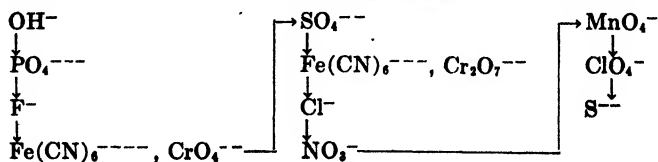
[324] G. M. SCHWAB has chosen to call this "developing," although this term has another meaning when used in connection with organic chromatography (see p. 592).

The resulting zones in the acid Al_2O_3 column are revealed by passing salt solutions that form characteristically colored salts with the respective anions through the column. There is not much choice here, since silver salts are practically the only ones that produce colored precipitates with several of the preceding assortment of anions.

Kubli[325] systematically compared a number of other anions with each of those studied by Schwab and Dattler and so constructed a more comprehensive series than that just given. The extended order for adsorption on an acid alumina column is:

$$OH^- \rightarrow PO_4^{---} \rightarrow C_2O_4^- \rightarrow F^- \rightarrow \begin{Bmatrix} SO_3^{--} \\ Fe(CN)_6^{----} \\ CrO_4^{--} \end{Bmatrix} \rightarrow S_2O_3^{--} \rightarrow SO_4^{--} \rightarrow$$

$$\rightarrow \begin{Bmatrix} Fe(CN)_6^{---} \\ Cr_2O_7^{--} \end{Bmatrix} \rightarrow \begin{Bmatrix} NO_2^- \\ CNS- \end{Bmatrix} \rightarrow I^- \rightarrow$$

$$\rightarrow Br^- \rightarrow Cl^- \rightarrow NO_3^- \rightarrow MnO_4^- \rightarrow ClO_4^- \rightarrow CH_3COO^- \rightarrow S^{--}$$
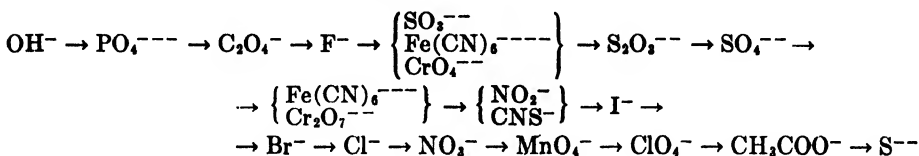
(It is difficult or impossible to distinguish a zonal or adsorption difference between the anions inclosed in brackets.)

The acid alumina is prepared by treating alumina that is suitable for cation adsorption, i.e., alkaline alumina, with approximately 1 N hydrochloric acid (or chloric acid).[325a] After washing, the material is dried. Alkali chloride (chlorate) is removed and acid is bound. The binding of the acid occurs on the surface of the Al_2O_3 and there leads to a quasi formation of basic aluminum chloride. This process, which, in the case of hydrochloric acid, leaves the interior of the adsorbent unchanged, can be represented schematically:

$$[Al(OH)_3]_x + HCl \rightarrow [Al(OH)_3]_{x-1}Al\begin{matrix} (OH)_2 \\ \\ Cl \end{matrix} + H_2O$$
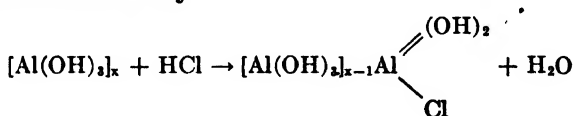
If this alumina, which is salified on its surface, comes in contact with an anion (Y) that is more firmly bound by aluminum than the chloride ion, the following reaction takes place:

$$[Al(OH)_3]_{(x-1)}Al\begin{matrix} (OH)_2 \\ \\ Cl \end{matrix} + Y^- \rightarrow [Al(OH)_3]_{(x-1)}Al\begin{matrix} (OH)_2 \\ \\ Y \end{matrix} + Cl^-$$
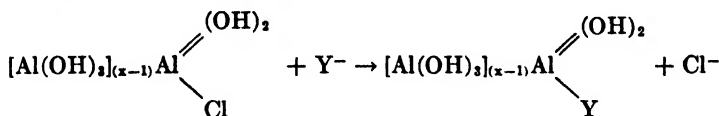
Hence, this presents a clear picture of an exchange adsorption, and the action of the acid alumina can also be termed that of an alumina-permutite. Accordingly, the order, i.e., the relative position of anions on the

[325] H. KUBLI, Helv. Chim. Acta 30, 453 (1947).

[325a] Compare H. FLOOD, Chem. Abstracts 38, 2895 (1944) regarding the use in anion-adsorption of filter paper impregnated with Al_2O_3 and treated with perchloric acid.

acid alumina column, can be regarded as a reflection of the increasing solubilities of the corresponding basic aluminum salts. An elution or removal of the anions from the column can be accomplished by all the means that lead to a reaction of basic aluminum salts. Hence, OH⁻ ions will be effective, since $[Al(OH)_3]_x$ will be regenerated, and likewise anions that stand higher in the adsorption series, that is, those that form less soluble basic aluminum salts will also serve. Finally, higher concentrations of the anion, which was initially bound on the column, will also be active. In the latter case, the eluting action is due to a reversal of the exchange reaction which led to the adsorption. Analogous considerations can also be set up for the adsorption of cations on a basic alumina column. It would then be assumed that alkali hydroxide is adsorbed in the form of aluminate on the surface of the alumina and reacts there with metal ions. This also would correspond to an ion exchange, i.e., of the K^+ or Na^+ ions of the aluminate. It is unlikely that the reaction product remains as aluminate in the phase association of the alumina. It is probable that hydrolysis will follow and thus the metal hydroxide will separate as a special phase. Possibly there is no intermediate formation of aluminate, but the original alumina surface functions as a donor of OH⁻ ions and the metal hydroxide formation occurs in solution. Since the alkali is much easier to remove from basic alumina by washing than are anions from acid alumina, the adsorptive character of the exchange is far more pronounced in the acid than in the basic alumina column.

The studies of inorganic chromatography by Schwab and his associates provide interesting glimpses into the process of exchange adsorption and, as shown by the findings cited here, they can serve as model instances for the investigation of this type of adsorption. In contrast to organic chromatography, which is particularly useful in the preparative isolation of materials, inorganic chromatography appears to be of little value in the isolation of salts; its chief utility lies in analytical separations. The decision as to whether inorganic chromatography should be used for practical analytical purposes should be made in the light of the objectives to be attained. The present writer believes that chromatographic separations offer few real advantages in systematic qualitative analysis, i.e., in the detection of the ingredients of a complicated mixture. Plenty of specific and selective tests, that are also sensitive, are now available, so that the constituents of a mixture can be detected simply and at good limiting proportions without any preliminary separation. A separation that precedes the actual identifying tests is never anything beyond an aid that must be resorted to merely because of the lack of detection reactions that can be applied directly to the original sample. When

such reactions are feasible, an antecedent separation is superfluous. The conditions are quite different when inorganic chromatography is applied in solving special problems in inorganic chemical analysis. This includes the separation of ingredients of certain binary mixtures, and especially the employment of inorganic chromatography in trace analysis. Local accumulation of material on the adsorption column combined with sensitive and selective reactions can be advantageously used in such circumstances. Thus Schwab and Ghosh (*loc. cit.* p. 600) showed that as little as 0.01γ of iron can be detected by the Prussian blue test after localized adsorption on an alumina column 1 mm. in diameter and 12 cm. long. Beaucourt and Masters[326] demonstrated that 1 part of iron accompanied by as much as 10,000 parts of chromium or cobalt can be detected by an analogous procedure. Extremely low identification limits are attained with numerous other cations if they are fixed beforehand in an adsorptive column.

Kubli (*loc. cit.*) found that after anions are fixed on an acid alumina column, their local detection by means of suitable color reactions is much more sensitive than the same tests carried out in the form of spot reactions on paper or on non-porous media. In fact, the reaction picture on the column (color tone and zone height) permits quantitative estimations.[326a] It appears that quantitative microanalytical determinations can be made by measuring a chromatogram, provided certain conditions are maintained (use of dilute solutions, same adsorption materials, *etc.*). These methods could be called chromatogrammetry.

A very interesting use of column adsorption is its employment in inorganic gravimetric analysis to remove interfering ions. Adsorbents other than alumina can also be used. Samuelson[326b] was the first to call attention to this and to make application of his finding. Kubli (*loc. cit.*) cites the following example. The presence of the anions interferes when the metals are to be determined in a solution which contains Fe^{+++}, Mg^{++}, SO_4^{--}, and PO_4^{---}. The cations interfere when the anions are to be determined. Hence, the common practice has been to use a carbonate precipitation to accomplish the necessary cation-anion separation. This operation is superfluous if the solution is passed through a column of alumina that has been pretreated with hydrochloric acid. The iron and magnesium are contained as chlorides in the issuing solution, which is entirely free of sulfate and phosphate. These anions are held

[326] J. H. BEAUCOURT and D. L. MASTERS, *Metallurgia* **32**, 181 (1945).

[326a] Compare P. JACOBS and F. TOMPKINS, *Trans. Faraday Soc.* **41**, 388, 395, 400 (1945).

[326b] O. SAMUELSON, *Z. anal. Chem.* **116**, 328 (1939); *Chem. Abstracts* **34**, 6539 (1940); **35**, 1340 (1941).

in the adsorption column because of ion exchange. The anions fixed in the column can be eluted by washing the alumina with dilute alkali; the total original anion content will then be in the issuing solution. A second example is the quantitative determination of potassium in its sulfate, phosphate, chromate, ferro- and ferricyanide. It is well known that these ions may not be present if the perchlorate or chloroplatinate methods are to be used, and they must be replaced by chloride or nitrate. Heretofore, tedious procedures were required to secure this replacement. However, the multivalent anions are easily held back through the ion exchange in an hydrochloric or nitric acid alumina column, and they are replaced, without loss of alkali, by chloride or nitrate ions. There is no doubt that many advantageous applications will be found in chemical analysis for such quantitative ion exchanges obtained by means of basic or acid adsorption columns.

It is probable that inorganic chromatography will prove susceptible to considerable extension in the field of metal analysis, especially if complex compounds and ions are taken into consideration and used sensibly. This wider field of application was indicated by the early observation by Schwab that complex formation produces a shift in the positions at which metals adhered to the adsorption column (see p. 602). Complex formation with organic partners seems to offer especially good prospects, because these reagents are quite prone to produce complex ions. The incorporation of metals in organic complexes provides a direct connection to organic chromatography, in which selective effects are especially evident. Inner complex compounds without electrolytic character, in which the inorganic nature is extensively repressed in comparison with the organic nature, appear to be especially apt subjects for chromatographic separations. Only one observation along this line has been available up to the present. This is the finding by Flood and Smedsaas[327] that an aqueous solution of the analogously constituted water-soluble inner complex salts of glycine with nickel and cobalt can be chromatographically separated on an alumina column. Preliminary studies of the chromatography of inner complex salts from their solutions in organic liquids have been made by Feigl and Suter.[328] They found that a chloroform solution of Cu and Ni benzoinoximate (see p. 266) produces a band of the copper salt on an Al_2O_3 column while the nickel salt is fixed some distance below. Similarly, the iron salt is adsorbed first and directly after it the copper salt from a chloroform solution of ferric and cupric oxinates (see p. 183). A solution of Cu and Zn dithizonates (see p. 241) in a mixture of chloroform (20%) and petroleum ether (80%) was

[327] H. Flood and A. Smedsaas, *Chem. Abstracts* **37**, 5334 (1943).
[328] F. Feigl and H. A. Suter, unpublished studies.

passed through a column, consisting of $CaCO_3$ above Al_2O_3. The copper dithizonate was fixed by the calcium carbonate and the zinc salt was adsorbed on the alumina. Hence, it appears that not only are solutions of inner complex salts in organic solvents susceptible to chromatography[329] but, in addition, the ingredients of a mixture of salts derived from the same complex-former can be separated chromatographically. Obviously, it should be possible to utilize this effect to heighten the selectivity and sensitivity of reactions that lead to the formation of inner complex salts which are soluble in organic liquids.

Erlenmeyer and his collaborators introduced a procedure that many regard as a further development of inorganic chromatography. He and Dahn found[330] that a number of metallic salts, when in water solution, are readily fixed on 8-hydroxyquinoline (I) or on mixtures of this reagent with nonadsorptive siliceous earth. Many ions form colored bands on such columns, and the separated compounds are thus easily located, even when only minute amounts are present. Trials with neutral solutions containing 2, 3, or 4 compounds have shown that the following ions form colored bands in the order given here, beginning at the top of the column:

VO_3^-	grey-black	$\rightarrow Bi^{+++}$	yellow	$\rightarrow Zn^{++}$	yellow
WO_4^{--}	yellow	Ni^{++}	green	Fe^{+++}	black
Cu^{++}	green	Co^{++}	reddish	UO_2^{++}	red-orange

The positions of iron and zinc are reversed if the fixation is made from an aqueous acetic acid solution. Development of the chromatogram with aqueous acetic acid facilitates the resolution of nickel and cobalt. The method is fairly sensitive; for example, 2γ of ferric iron can be detected. It has been suggested that this procedure may be adaptable to the semi-quantitative analysis of alloys.

Erlenmeyer and Schoenàuer[331] studied the passage of a solution containing K, Ca, Mg, and Na acetates through a column of water-insoluble, pulverized violuric acid (II). The corresponding metal violurates were formed and retained as a succession of colored bands—violet, red, brick-

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[329] The interesting findings of A. KORINSFASKY [*Chem. Abstracts* **40**, 2405 (1946)] should be noted in this connection. He observed that the various colored metal compounds deposit in definite zones when ether, amyl alcohol, or chloroform solutions of ferric thiocyanate, vanadium oxinate, and copper diphenylcarbazone undergo capillary ascent in strips of filter paper. The sensitivities of tests that are based on the formation of these metal salts can thus be increased decidedly. In view of the fact that capillary pictures on paper and chromatography both involve the same phenomenon, namely adsorption, there can be little doubt that tests will show that the compounds studied by Korinsfasky can be fixed chromatographically from their solutions in organic liquids.

[330] H. ERLENMEYER and H. DAHN, *Helv. Chim. Acta* **22**, 1369 (1939).

[331] H. ERLENMEYER and W. SCHOENAUER, *Helv. Chim. Acta* **24**, 878 (1941).

red, and red-violet, respectively.   The separation into zones is especially evident with binary mixtures of acetates; for instance, sodium is easily detected in the presence of potassium.   Erlenmeyer and Schmidlin[332] passed a solution of potassium and sodium acetate through a column, consisting of 5-oxo-4-oximino-3-phenylisoxazoline (III) above and violuric acid below (both mixed with starch).   The colored potassium and sodium salts of (III) were formed initially in the upper part of the adsorbent.   When water was then sent through the column, the more readily soluble sodium salt was carried along, and produced a band of red-violet sodium violurate in the lower part of the column.   The yellow potassium salt of the isoxazoline remained in the upper portion of the column.   This separation can be accomplished on a micro scale.   The same is true of the other separations cited here, on columns prepared from (I), (II), or (III), which, in accord with their acidic character, are salt-forming.
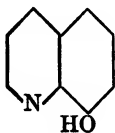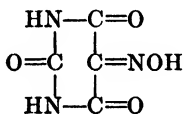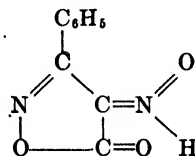
(I)   (II)   (III)

There is no doubt that the technic described by Erlenmeyer has analytical value or that it is capable of extension.   However, it is hardly fitting to call it chromatography in the sense of its being an adsorption analysis.   Although the apparatus used is that commonly employed in chromatographic methods and though it also results in the production of zones in the columns, these similarities should not lead to the false conclusion that this is an adsorption method.   According to definition, and also experience, adsorption requires that a material serving as an adsorbent shall react or be active only until an equilibrium is reached. The latter is determined by the free surface, or by the quantity of compounds or ions that can be displaced from the surface (addition and exchange adsorption).   These requirements are not met by (I) to (III), because, theoretically, the whole of these compounds can enter into complete reaction with metal compounds to form their respective salts. Consequently, the Erlenmeyer technic is really concerned with fractional precipitations, that occur when a salt solution flows by a difficultly water-soluble reagent.   This process corresponds, in all respects, to the passage of a mixed solution through the capillary spaces of a filter paper that has been impregnated with certain reagents.   In the latter

[332] H. ERLENMEYER and J. SCHMIDLIN, Helv. Chim. Acta 24, 1213 (1941).

case also, there may be separate reaction zones of the respective solutes. Such possibilities have been known for a long time and are often used in spot test analysis.

At the beginning of this discussion of Tswett chromatography it was pointed out that its essential feature, the streaming of a solution through an adsorbent, also holds for the Goppelsroeder capillary analysis. The formation of zones in the adsorbing column corresponds to the various capillary heights of ascent of the constituents of a solution when the latter rises in a strip of filter paper. It is evident that the adsorption capacity of filter paper is usually less than that of an adsorption column composed of a solid material. This is particularly true when it is not the cellulose, as such, which acts as the adsorbent, but rather the mineral substances that are contained in it. However, the adsorption effect of a column can be extensively conferred on paper if the material of the column is incorporated in the filter paper.` This has been demonstrated by Flood,[332a] who used an alumina adsorption paper. The latter is prepared by impregnating filter paper with a solution of an alkali aluminate, drying, treating with sodium bicarbonate, washing, and finally drying again. If water is allowed to rise in such paper and then a solution of a salt, the same zones are obtained as when the salt solution percolates through a column of basic alumina. By treatment with acid, it is also possible to prepare acid alumina adsorption papers, which are suitable for the separation of anions. Hopf[332b] carried out spot reactions on basic alumina papers and also on papers impregnated with starch plus suitable reagents (oxine, violuric acid, etc.). He found that colored reaction products are formed in different zones of the fleck. He assumes that there is primarily an adsorption of cations on the alumina (starch), and that the reagent present then acts as developer for the chromatogram that is made up of the adsorption zones. The present writer does not believe it probable that the reagent incorporated in an adsorption paper, and present in excess, acts solely as developer for the previously formed adsorption zones. It is always necessary, and predominantly, to take into account a direct reaction of the kind that occurs so often with impregnated filter papers in spot tests. The zone formation observed by Hopf may be due to fractional precipitation combined with a buffering action due to the basic alumina. (In the case of oxine, an activity of the aluminum oxinate may be involved.) Such zone formations resulting from fractional precipitations have nothing to do with the purely adsorptive zone formation of chromatography. The term chromatographic spot test proposed by Hopf, should be reserved for spot reactions in which

[332a] H. FLOOD, Z. anal. Chem. 120, 327 (1940).
[332b] P. P. HOPF, J. Chem. Soc. (London) 1946, 785.

it is certain that there has been a preceding chromatographic separation.

As indicated by the statements in this section, the terms chromatography, chromatogram, chromatographic analysis, *etc.*, are often employed in a sense that does not agree with the meaning originally introduced by Tswett. The reason for this change in meaning is that the elements of Tswett's procedure, namely the adsorption, the production of zones, and the use of adsorption columns, were regarded as characteristic in themselves and divorced from their connection with each other. To arrive at a correct and rational terminology, it would be well to designate the methods of separating materials and isolation, which are based on the principle discovered by Tswett, as column adsorption or Tswett's adsorption separation. The term chromatography should be reserved for those instances in which the zones produced by column adsorption are directly recognizable, either through their own colors (in visible or ultraviolet light) or which can be made apparent by the action of suitable reagents (passage of a reagent solution or spotting) and if an analytical goal is reached by means of this visibility or development. Adsorption zones that have a color themselves or that have their colors developed by a suitable treatment, are true chromatograms. Their evaluation for quantitative purposes constitutes chromatogrammetry.

Foaming Analysis

It was indicated on p. 519 that materials dissolved in water accumulate in foams and at the interfaces of emulsions, *i.e.*, on free liquid surfaces. By definition, such localization is adsorption. If this type of adsorption occurs to a sufficient extent, it is theoretically possible to bring about a separation of materials by this means. In other words, a gas could be blown through a solution to produce an artificial froth, and the latter could be mechanically separated from the non-foaming part of the liquid. Foams break, *i.e.*, they are reconverted to liquid on more or less prolonged standing, or they can be made to do so quickly by adding small quantities of materials that lower their surface tensions. If this is done, a solution can be divided into a "spumate," in which certain materials which were previously distributed homogeneously are localized, and the corresponding residue. This type of separation, in which a foam acts as the adsorption system, is called "foaming analysis." Talmud and Pochil[333] were the first to suggest the practical application of separations by the aid of foams. They treated the saturated juice obtained in beet sugar manufacture with milk of lime and then blew air through the liquid. The result was a vigorous foaming, that stopped after a while.

[333] D. TALMUD and P. POCHIL, *Kolloid-Z.* **61**, 101 (1932).

According to Ostwald and Siehr[334] it is possible to remove in this foam, materials which, even in small amounts, interfere with the crystallization of the sugar. Ostwald and his students[335] made a systematic study of foaming analysis. They described apparatus for producing foams, and also for the refoaming of the spumate, a procedure that results in more precise separations. A simple apparatus, that can be constructed from the equipment ordinarily at hand was described by Hesse.[336]

Foaming analysis, like all the other adsorption analyses described in the preceding discussion, is primarily a method of separation. An idea of the completeness that can be attained by the foaming procedure was given by Ostwald and Siehr.[337] They slowly passed nitrogen through 300 ml. of a solution (0.1%) containing a mixture of patent blue and new coccine. The violet mixed color could be seen in the foam zone directly above the surface of the liquid; and from there upward, the color changed more and more to blue. The liquid which foamed over (spumate) was pure blue, while the residue was red. Spectroscopic examination showed the residue to be practically free of patent blue, and only traces of new coccine were detected in the spumate. Other foam separations accomplished by these workers are: the division of colloidal solutions of congo rubin into fractions of different degrees of dispersity; the complete dealbuminization of urine; the separation of albuminous materials from the amniotic fluid of potatoes. Mischke[338] studied the composition of the foam in contrast to that of whole beer and found that albumoses, dextrins, and hop resins accumulate in the foam and determine its special taste. These materials are also responsible for the foaming ability. Courrier and Dognon[339] demonstrated the accumulation of sex hormones in foams.

Foaming analysis is the most recent branch of the separation of materials by means of adsorption. Consequently, relatively little experimental material concerning it is available as yet. Its application obviously will be restricted to those materials whose solutions can be made to foam. Accordingly, there is little possibility that foam separations will attain an analytical importance comparable to that of capillary analysis, spot testing, and chromatographic analysis. Nevertheless, special cases will assuredly arise in which it may offer notable advantages. It should also be remembered in this connection that it is extremely

[334] Wo. Ostwald and A. Siehr, *Kolloid-Z.* **79**, 15 (1937).

[335] A. Siehr has made studies on the theory of foam. Compare *Kolloid-Z.* **77**, 27 (1936); **78**, 156 (1937); **85**, 70 (1938).

[336] G. Hesse, Adsorptionsmethoden in chemischen Laboratorium, Berlin, 1943.

[337] Wo. Ostwald and A. Siehr, *Kolloid-Z.* **76**, 38 (1936).

[338] M. Mischke, *Kolloid-Z.* **90**, 77 (1940).

[339] R. Courrier and A. Dognon, *Compt. rend.* **209**, 242 (1939).

difficult to concentrate foaming solutions by boiling them down, and that such concentration is not permissible with heat-sensitive materials. In such cases, the formation and separation of a spurnate may be of interest. Perhaps it will be possible to extend the field of application of foam analysis by adding foam-promoting materials, such as peptone, saponin, *etc.*, to the sample.[340]

In connection with the accumulation of the dissolved materials of aqueous solutions in the interface between the water and air (foams) or water and immiscible liquids (emulsions), it is appropriate to call attention to the interesting observations made by Zocher and Török.[341] They found that when a dilute water solution of berberin sulfate is shaken with benzene, toluene, chloroform, *etc.*, the original weak yellowish fluorescence is changed into a strong yellow fluorescence. The latter disappears when the emulsion breaks, but is regenerated if the system is shaken. This phenomenon obviously involves factors analogous to those operating in the experiments made by Deutsch (see p. 520). The equilibrium prevailing in the water solution between the non-fluorescing and fluorescing isomers of berberin sulfate, is shifted in the water-benzene (*etc.*) interface toward the side of the fluorescing form. This shift corresponds to a preferential adsorption of the fluorescing form. Hence, there is a possibility of making analytical use of such equilibrium shifts of fluorescing compounds (or perhaps also of materials that are colored in daylight) in order to increase the sensitivity of tests.

[340] Wo. OSTWALD and M. MISCHKE, *Kolloid-Z.* **90**, 205 (1940).
[341] H. W. ZOCHER and C. TÖRÖK, unpublished studies.

Genetic Formation of Materials and Topochemical Reactions

If the formation of materials by chemical means involved nothing beyond the mere reaction, then any chemical process, which is accomplished in accord with its stoichiometric formulation, would invariably lead to products of the same form-species, color, solubility, *etc.* Experience has repeatedly demonstrated that this is not always true. Although an equation represents the most important part of a chemical event, nevertheless, it cannot portray everything that happens in the course of the formation of a material. For instance, it is well known that the beginning and the end of a precipitation process are not the only things which are influenced by variation of the attendant conditions, *e.g.*, concentration, temperature, pH, nature and concentration of the cosolutes, mixing, and the order of adding the materials. Sometimes products of different form-species and grain size, occasionally also of different color and solubility, result. Furthermore, side reactions that could not have been foreseen occur and to varying extents. These facts demonstrate that, in addition to a chemical main reaction, other chemical and physical factors have a decided share in the production of materials and can influence their properties. For these reasons, *every chemical production of a substance must be regarded* as *the net result of the concurrent action of all the chemical and physical relationships that function during the formation process.* A particular division of chemistry deals with tracing back the specific forms to definite chemical-physical conditions. V. Kohlschütter (1874–1939), a pioneer in this field of investigation,[1] coined the apt terms "chemistry of aggregation forms" and "the genetic formation of materials."

Examples of the effects of the particular conditions attending the formation of a solid material on its external appearance as well as on its physical and chemical behavior are to be found not only among changes occurring in solutions and resulting in the production of solid phases (precipitation reactions, electroylic depositions), but also in certain thermal decompositions of solids in contact with air. It should be noted that, in general, there is a range within which a variation of the experimental conditions produces no visible alterations in the properties of the resulting products. However, exceptions to this rule are known. Phenomena of the genetic formation of materials can have analytical significance in so far as they affect the selectivity and sensitivity of tests. The

[1] Compare biography in *Helv. Chim. Acta* **22**, 1059 (1939).

purity and form-species of precipitated products play an important part in quantitative analysis, especially in gravimetric and nephelometric procedures. The influences of the genetic factors are most readily discerned and perhaps have especially marked consequences in their effect on the degree of dispersion and associated properties of newly produced solid phases. Several characteristic examples will be given.

It has long been known that the metallic iron produced by heating iron oxalate is so finely divided that it glows when exposed to the air (pyrophoric iron). The analogous formation of pyrophoric lead by the thermal decomposition of lead tartrate was discovered by Alexander.[1a] These examples are chosen because they show plainly that the marked reactivity of these solids towards gaseous reactants depends on the extensive surface resulting from the particular conditions surrounding the preparation of these specimens or varieties. Compact masses of iron and lead are quite resistant to air. Another observation, that can also be considered as a phenomenon related to the genetic formation of a material, is the fact that the volume of the Cr_2O_3, when produced by heating ammonium bichromate, is many hundred times as great, and its color a much deeper green, than that of specimens of this oxide prepared by calcination of $Cr_2O_3 \cdot aq$ produced in the wet way. Kohlschütter and Tuescher[2] showed that lime prepared by heating calcium oxalate to red heat has a larger internal surface and forms milk of lime more readily than CaO obtained by igniting $CaCO_3$. In both cases, the lime retains the crystal form of the starting material (pseudomorphism). Another clear example of the dependence of the properties of an oxide on those of the original material from which it is produced by thermal decomposition was given by Kohlschütter and Frey.[3] Thorium oxide obtained by heating the oxalate readily forms colloidal solutions. This is not true of ThO_2 produced by igniting hydrous thorium oxide, sulfate, or nitrate. Likewise, the properties of the magnesium oxide obtained by calcining magnesium compounds depend, to a great extent, on those of the parent material.[4]

The influences of genetic factors in precipitation reactions are more common, more marked, and also of greater analytical importance. Before discussing precipitation reactions in which the starting materials are present in solution, reference should be made to other findings of Kohlschütter and Tuescher (loc. cit.). They observed that when crystals of basic copper sulfate, normal sulfate, and alkali double sulfate are

[1a] J. ALEXANDER, Colloid Chemistry, Vol. 3, p. 252. New York, 1931.
[2] V. KOHLSCHÜTTER and H. TUESCHER, Z. anorg. allgem. Chem. 111, 193 (1920)
[3] V. KOHLSCHÜTTER and A. FREY, Z. Elektrochem. 22, 1145 (1916).
[4] Compare M. LE BLANC and K. RICHTER, Z. physik. Chem. 107, 357 (1924).

treated with a basic solution, all three compounds are transformed into $Cu(OH)_2$, with retention of the original crystal form. However, the familiar change of the blue-green $Cu(OH)_2$ into black CuO proceeds at quite different rates in the three cases. The dehydration of the third of these pseudomorphs is rapid, that of the second is slower, while the first scarcely changes. Accordingly, the internal degree of dispersion intensively affects the course of this dehydration.

Excellent examples of the influence of the genetic factors in the production of materials are provided by precipitated hydrated ferric oxide, $Fe_2O_3 \cdot xH_2O$. In the normal precipitation, occasioned by the addition of alkali hydroxide or ammonia to ferric solutions, a gelatinous, voluminous precipitate appears. However, by varying the conditions under which the precipitation is made, it is possible to obtain hydrous oxides, and subsequent oxides, of ferric iron that have entirely different properties, which may be quite desirable from the standpoint of the analyst. Thus Hahn and Hertrich[5] showed that treatment of ferric solutions with sodium thiosulfate and potassium iodate produces a dense, highly pulverulent, bright yellowish red precipitate:

$$2Fe^{+++} + 2S_2O_3^{--} \rightarrow 2Fe^{++} + S_4O_6^{--}$$
$$2Fe^{++} + 3H_2O + IO_3^- + 4S_2O_3^{--} \rightarrow 2Fe(OH)_3 + I^- + 2S_4O_6^{--}$$
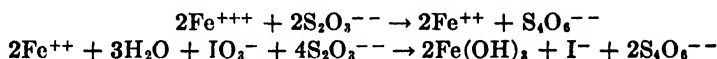
A 9 cm. filter paper easily accommodates 0.5 g. of this product, whereas the precipitate formed by the usual hydroxide reaction requires a much larger paper, and the filtration time is much longer. The precipitate obtained from a solution containing thiosulfate is only partially hydrated; its water content is less than that demanded by the formula $Fe(OH)_3$ ($= Fe_2O_3 \cdot 3H_2O$). The fact that this material, in contrast to normally precipitated ferric hydroxide, is resistant to boiling dilute nitric acid is in accord with this lower water content. Jannasch and Ruehl[6] observed that the ignition product of the precipitate produced by alkali from ferric solutions containing hydroxylamine hydrochloride remains soluble in dilute acids, even after protracted ignition. The fact that an acid-soluble ferric oxide can be obtained by suitable preparative conditions has made it possible to use a product of this kind (Brand's ferric oxide) as a primary standard for permanganate solutions. Rabe[6a] found that $Tl_2O_3 \cdot aq$ precipitated at room temperature by the action of hydrogen peroxide on solutions of $TlOH$ is dark brown and flocculent, whereas the product precipitated at 80–100°C. is black and sandy. The brown form is more readily soluble in dilute acids than the black variety, and like-

[5] F. L. HAHN and M. HERTRICH, Ber. 56, 1729 (1923).
[6] P. JANNASCH and F. RUEHL, J. prakt. Chem. 72, 2 (1905).
[6a] O. RABE, Z. anorg. allgem. Chem. 48, 427 (1906); 50, 158 (1906).

wise is more readily reduced by boiling water. It is also rather remarkable that the brown product requires heating to 500°C. before it acquires the properties of the black variety.

This discussion of the dependence of the properties of precipitated materials on the particular precipitation conditions must include a consideration of a phenomenon that likewise is involved in the genetic formation of materials. This concerns the fact that the properties of precipitates are dependent not only on the conditions that obtain during the precipitation, but also that a newly formed precipitate undergoes, with the passage of time, a more or less extensive alteration in its properties without the intervention of external influences. This process is known as aging. Examples of aging have been given in Chapter X in the discussion of the changes of condition in colloid systems in connection with the aggregation of particles. Likewise, in Chapter X, it was pointed out that the adsorption ability of precipitates can decrease with time. This change is evidenced by the observation that materials which are taken up during the formation of a precipitate may be partially released when the precipitate stands. Since it is known that the extent of every adsorption is very definitely related to the extent of the surface, the reversal of adsorption clearly indicates the nature of the essential change that occurs during aging. It is a diminution, with time, of the surface, and is accompanied by a change in the structure of the precipitate. This decrease in surface when crystalline preparations are recrystallized into coarser crystals (the so-called Ostwald ripening) can often be recognized by microscopic examination and direct measurement. The decrease in surface in such cases comes about through solution of the finer crystals, which thus contribute to the further growth of the larger crystals that are already present. However, as Kolthoff[7] has shown very clearly, such recrystallization that results in larger crystals is not the only process that occurs. It is also necessary to consider the fact that poorly developed crystals may undergo recrystallization into more perfectly formed crystals without notable increase in size.

Aging is by no means limited to precipitates that are crystalline from the start. In fact, structural changes that occur with time are to be expected particularly among amorphous precipitates[8] which frequently are a preceding stage of fine crystalline precipitates and therefore are

[7] I. M. KOLTHOFF, *Z. anal. Chem.* **104**, 331 (1936).
[8] The crystalline condition is characterized by an orderly spatial arrangement of the building units (molecules, atoms, ions) to form a lattice. This arrangement can often be revealed by X-ray interferences, even though no indication of crystallinity (crystal form, double refraction, *etc.*) is apparent under the microscope. In the latter case, the precipitates are said to be microscopically amorphous.

even more distant from a coarse crystalline end-condition. Actually, marked aging phenomena were first observed among gelatinous, slimy precipitates, such as the products of the hydroxide precipitation of multivalent metals. As a rule, the composition of such precipitates does not conform to the given hydroxide or oxyhydrate formulas, but contain far more water. Hence the terms "hydrous hydroxides," "hydrous oxides," "hydrated oxides" are quite apropos.[9]

Most of the water of the hydrous oxides and hydroxides is not bound constitutively, like water of hydration or crystallization, for instance. Rather, the main part of it is adsorbed; and some is occluded, *i.e.*, mechanically enclosed in the cavities of the precipitate. Consequently, every diminution of the surface must be accompanied by a release of adsorbed water, and usually also of occluded water. Structural changes may result from such dehydration processes even before a transformation into a crystalline form can be established, because the agglomeration of fine amorphous into coarse amorphous particles can doubtless also be regarded as a fundamental alteration of structure. Many oxyhydrates, which separate initially in an amorphous form, pass over to a crystalline condition on standing. This transformation, which is a result of aging, has been demonstrated to occur by the appearance of Röntgen interferences.

The foregoing remarks show that the aging of precipitates is a process that proceeds through intermediate stages from energy-richer to energy-poorer forms. Consequently, it occurs spontaneously, *i.e.*, without introduction of energy. Sometimes, an aging is apparent from a directly visible change in structure and the accompanying physical properties, such as altered color, different behavior in sedimentation, double refraction, *etc.* However, the aging is revealed more often by a decreased reactivity of precipitates. This can show up as a lowered adsorbability or peptizability, or in a sluggish or even complete lack of reactivity toward acids, alkalies, or other reagents.

The hydroxide precipitation of indium and rare earth metals exemplifies a change in structure that can be directly established quite soon after the precipitate is thrown down. The precipitates are quite slimy at first, but when warmed in the reaction liquor they change more or less quickly into a dense form which filters well.[10] The same is true of the

[9] H. B. WEISER, The Hydrous Oxides and Hydroxides, Vol. 2, of Inorganic Colloid Chemistry, New York, 1935. This excellent book contains a large number of statements concerning the aging of the products obtained by hydroxide precipitations.

[10] Many writers in analytical publications unjustifiably designate such changes in structure as "becoming crystalline" without any exact examination, under the microscope, for instance. It should be stressed that satisfactory filtrability alone is no guarantee of crystallinity.

fluoride precipitates of the rare earths. Similarly, their initial cheesy oxalate precipitates rapidly become dense when warmed.

Among amorphous precipitates, aging is most plainly revealed by the change in reactivity. It has long been known that hydrous oxides, precipitated by adding OH^- ions to salt solutions, particularly of tri- and quadrivalent metals, on standing become resistant to dilute acids. Likewise, aged amphoteric hydrated oxides do not dissolve well in alkalies. When the solubility characteristics of aged precipitates are being tested, note should be taken not only of differences exhibited toward various concentrations of acids (alkalies) but also of differences, which often are quite characteristic, that appear when the period of exposure to the acid (base) is varied. In such studies, it is frequently hard to determine whether the differences displayed by aged precipitates are due to a decreased solubility or to a lowered rate of solution. As a rule, both may be expected. Decreasing solubility as well as slower rate of solution can be regarded as a solution anomaly. However, such solution anomalies in the case of precipitates that have aged, either in isolated form or in contact with the reaction medium, can be displayed to markedly different extents. The chemical composition of the precipitate and its history, *i.e.*, the precipitation conditions, play a determining role. In general, the rate of aging is greater at the start than it is later; also it is greater at elevated temperatures. Accordingly, aging effects can be established most definitely if the behavior of a precipitate can be compared with a specimen *in statu nascendi*. This can be done in the case of palladous hydroxide. If an excess of sodium hydroxide is added to a solution of a palladium salt, no precipitate appears. Instead, a yellow solution is formed due to the immediate solution of the hydroxide to produce $Na_2[Pd(OH)_4]$. If, however, the base is added drop by drop, so that brown $Pd(OH)_2$ precipitates at first, and then the rest of the alkali is introduced immediately, or after various periods of waiting, different amounts of the precipitate remain undissolved.[11]

As was pointed out, amorphous precipitates can become crystalline on aging, but the necessary time can be quite long. Thus, hydrous chromic oxide is amorphous and remains so for years at room temperature. Nevertheless, Klanfer and Pavelka[12] found that an aging of this compound can be definitely established within a few hours or days, as shown by a decrease in its solubility in acids. Attention is again directed to the other examples of aging given in Chapter X. A further instance is the behavior of the amorphous ferric salt of bis-*p*-chlorophenylphosphoric acid (see Chapter VI). The precipitate thrown down at room

[11] F. Feigl, unpublished studies. Compare also L. Wöhler and J. König, Z. anorg. allgem. Chem. **46**, 323 (1905).

[12] K. Klanfer and F. Pavelka, Kolloid-Z. **57**, 324 (1931).

temperature is soluble in 2% hydrochloric acid, in contrast to aged preparations which require more concentrated acid for their dissolution. Most of the instances of aging of precipitates have been discovered and studied with respect to their behavior toward 'acids and bases. However, the action of hydrous alumina toward pyrocatechol and ammonia (see p. 362) shows that the activity of complex-formers can also be drawn on in experimental investigations of aging.

In view of the fact that freshly formed precipitates are immediately subjected to aging, it must certainly be assumed that precipitates which are produced in analytical practices, or which are treated in such procedures, have already undergone at least some aging. There is no doubt that certain steps in many analytical procedures are designed to promote aging. Examples are: lengthy warming after precipitation; allowing precipitates to settle; judicious choice of the amount and concentration of acids or bases for taking precipitates into solution. Many widely used procedures, such as colorimetric determinations employing protective colloids, and the collector action of precipitating materials or of freshly prepared precipitates, which is now coming into wide use in trace analysis, obviously involve useful applications of precipitates that have aged little if any. Accordingly, aging is of interest not merely as one of the phenomena of the genetic formation of materials, but it also has considerable significance for the theory and practice of analytical chemistry.

Metal sulfides furnish numerous instances of the dependence of the properties of precipitated materials on the details of their production. For example, manganous sulfide, obtained in the course of a qualitative analysis, sometimes comes down in a flesh-colored form which is rich in water, and sometimes as an olive-green dense precipitate. Seeligmann[13] proved that the green variety can always be precipitated if much free ammonia and the minimum quantity of ammonium salts are present. Moser and Behr[14] studied the precipitation of metals of the $(NH_4)_2S$ group by compressed hydrogen sulfide. They found that zinc sulfide, when formed under pressure, does not dissolve in dilute mineral acids. The same is partly true of iron sulfide. It is further known that the value of the solubility product of heavy metal sulfides can vary according to whether the precipitation is carried out with H_2S, NaHS, or Na_2S. This was shown for the sulfides of lead, silver, and copper by Jellinek and Czerwinski,[15] and for zinc sulfide by Glixelli.[16] Zinc sulfide produced

[13] F. Seeligmann, Z. anal. Chem. **53**, 594 (1914).

[14] L. Moser and M. Behr, Z. anorg. allgem. Chem. **134**, 491 (1924); compare G. Bruni and M. Padua, J. Chem. Soc. Abstracts **90**, 157 (1906).

[15] K. Jellinek and J. Czerwinski, Z. physik. Chem. **102**, 476 (1922).

[16] S. Glixelli, Z. anorg. allgem. Chem. **55**, 297 (1907).

from alkaline solution dissolves 4–6 times more in dilute acids than when formed by hydrogen sulfide from acid solutions.

It is also remarkable that PtS₂ precipitated in the cold is easily soluble in warm nitric acid, whereas, if this sulfide is thrown down from a warm solution, it is attacked by the acid with difficulty.[16a] The divergent solubility characteristics of metal sulfides precipitated at different pH values are frequently ascribed to differences in particle size. Smaller particles invariably are more soluble in water than coarser particles (see p. 433), and since solution processes in acids proceed *via* the dissolved portions, this explanation seems plausible; it may also hold for the solubility differences exhibited by platinum sulfide toward nitric acid. However, the formation of various modifications of sulfides cannot be excluded. This is certainly the case with manganous sulfide, whose green and flesh-colored modifications do not represent mere differences in particle size; they surely are distinct varieties of this sulfide.

It should be noted that genetic factors attending precipitations manifest themselves not only in the properties of the products but also at their actual formation. One of the most impressive instances of the significance of the precipitation conditions can be found in the formation and behavior of cobalt and nickel sulfides. All of the systematic schemes of qualitative inorganic analysis make practical use of the well known fact that these sulfides cannot be precipitated from acid solution, but if they are once thrown down from ammoniacal solution, they are resistant to dilute mineral acids. Thiel and Gessner[17] have shown that the reason for this anomaly is probably to be found in the fact that nickel sulfide occurs in three distinct modifications, namely α-, β-, and γ-NiS. The α- and β-modifications are soluble in 2 N HCl, but to different degrees, the α-form being more soluble. The γ-form is insoluble in 2 N HCl and this modification forms rapidly in alkaline solution. Analogous modifications of cobalt sulfide can be assumed. Nickel cyanide behaves similarly to nickel sulfide. It cannot be produced in acid solution, but once formed by treating a neutral nickel solution with alkali cyanide, or by acidifying a solution of Na₂[Ni(CN)₄], it is resistant to dilute acids. Feigl and his associates[18] showed that good evidence can be advanced (see p. 102) for regarding nickel cyanide as Ni[Ni(CN)₄], *i.e.*, as the stable nickel salt of the unstable acid H₂[Ni(CN)₄]. Accordingly, it is logical to suppose that in an acidified solution the production of hydro-

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[16a] Compare TH. W. FRESENIUS, Anleitung zur qualitativen chemischen Analyse, p. 290, Brunswick, 1919.

[17] A. THIEL and H. GESSNER, *Z. anorg. allgem. Chem.* **86**, 1 (1914); A. THIEL and H. OHL, *ibid.* **61**, 369 (1909).

[18] F. FEIGL, V. DEMANT and E. DE OLIVEIRA, *Anales asoc. quim. Brasil* **3**, 72 (1944).

nickelocyanic acid, or $[Ni(CN)_4]^{--}$ ions, will be so slight that there will not be a rapid precipitation of the nickel salt.

Feigl and Raacke[19] have found that lead molybdate exhibits a remarkable solution anomaly. This salt comes down as a white precipitate in acetic acid solution when Pb^{++} and MoO_4^{--} ions are brought together. If hydrogen peroxide is also present, the precipitation is completely prevented because of the production of MoO_5^{--} ions. Consequently, it is logical to expect $PbMoO_4$ to be soluble in acetic acid-hydrogen peroxide. However, solution does not occur; not a trace of the lead salt dissolves, even on protracted boiling. Böttger[19a] states that lead thiosulfate immediately after being precipitated is soluble in dilute acetic acid, and on long standing is again deposited from this solution. In contrast, aged PbS_2O_3 is insoluble in dilute acetic acid.

The obvious anomaly, that certain compounds, once they have been produced, are insoluble in lower pH ranges, even though they cannot be precipitated at these same pH values, is also encountered among inner complex salts. Most inner complex salts act quite normally as regards their precipitability and dissolution; in other words, these processes are definitely related to certain pH values. An interesting analytical employment of such pH dependence in connection with inner complex Ni-dimethylglyoximate is discussed on p. 661. A marked solution or precipitation anomaly occurs with inner complex salts when the aqueous, alcohol, or acetone, *etc.*, solution of the particular precipitant contains chiefly the inactive pseudo aci- (or baso-) form in equilibrium with an aci- (baso-) form that is capable of forming a salt. This interesting fact indicates certain common causes for the observed anomalies. First of all, it might be thought that this tautomeric equilibrium, which is shifted toward the aci-form with rising pH, might be sluggishly established. However this postulate cannot be maintained since, actually, the conversion of the pseudo aci- into the aci-form and *vice versa* proceeds very rapidly. This is evidenced by the speed at which alkalies dissolve the water-insoluble pseudo aci-forms, and their prompt reprecipitation when these solutions are acidified. Consequently, another reason must be sought to account for the failure of the equilibrium system to undergo the expected precipitation or dissolution. However, it is not clear as to which of the two processes really does not take place. Accordingly, it is not known whether in one case the solubility product is exceeded but the precipitate nevertheless does not form, or whether, in the other case, the solubility product is not reached and the precipitate that has been formed nonetheless does not go into solution. The former type of disequilib-

[19] F. FEIGL and I. D. RAACKE, *Anal. Chim. Acta* **1**, 317 (1947).

[19a] W. BÖTTGER, Qualitative Analyse, 7th ed., p. 333, Leipzig, 1925.

rium, *i.e.*, the production of an extremely stable supersaturated solution, is observed more often, and hence is a more familiar occurrence. It will be pointed out later that the formation of supersaturated solutions is connected with the fact that the production of nuclei and their growth, *i.e.*, the factors which govern the development of a new phase, may proceed quite slowly.[20] However, the possibility cannot be excluded that the equilibrium may be exceeded in the opposite direction. In other words, a solid may persist for a long time in contact with a solvent that is far from saturated with respect to this solid. Solution anomalies were pointed out in the discussion of the aging phenomena of heavy metal hydroxides and other precipitates. Remarkably, these materials are always microscopic amorphous precipitates. Such cases involve a reaction sluggishness which increases with the time that has elapsed before the precipitate is subjected to the particular dissolution reagent. It is characteristic in such instances that the quantity of precipitate carried into solution by treatment with acid or base depends also on the period of exposure to the dissolution agent.

Aging is assumed to be the reflection of a decrease in the free reactable surface of the precipitate. In some cases, there is also transformation into energy-poorer modifications. Some inner complex salts display a solution anomaly that seems to be of a type which differs fundamentally from that which has just been discussed. In these cases even the freshly precipitated material is practically insoluble at certain pH values, and hence there can be little likelihood of an alteration of the precipitate with time.

A better understanding of extremely sluggish solution and precipitation processes can perhaps be obtained if it is remembered that there may be a difference in the constitution of molecules in the dissolved as compared with the solid state, and that a change of constitution may intervene as a separate step in the total process of the deposition and dissolution of a precipitate. The change in constitution, which perhaps (in contrast to aging) occurs in solution, may consist of (1) intramolecular rearrangement (isomerization, including conversion of a true salt into a pseudo salt), (2) a polymerization, or possibly (3) of a change in hydration. If this alteration does not take place instantaneously, but pro-

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[20] Numerous readily soluble salts, that carry water of crystallization, when melted in the latter and then cooled, form very stable solutions, and sometimes even glasses. Familiar examples are sodium thiosulfate, acetate, *etc.* Even more difficultly soluble salts, *e.g.*, gypsum and magnesium oxalate, readily form supersaturated solutions. For instance, four-fold supersaturated solutions of the latter stay clear for weeks, and ten-fold as long as forty hours [W. M. FISCHER, *Z. anorg. allgem. Chem.* **153**, 66 (1926)]. Among very slightly soluble compounds, supersaturated solutions play a part in the region of uncertain reactions (see Chapter II).

ceeds slowly, it will determine the rate of solution or deposition. Both processes can thus be retarded in such manner that the phenomenon of a false equilibrium appears. Among the solution anomalies discussed here, false equilibria are observed only in acid medium, whereas the precipitation proceeds rapidly at higher pH values. Such findings suggest that OH^- ions catalytically hasten the changes in constitution assumed here. These catalyzing ions are absent in acid solution, and accordingly in such surroundings the precipitation or solution proceeds so slowly that an impression of non-reactivity is obtained. Similar considerations can be adduced to explain false equilibria in other precipitation reactions, especially the aforementioned anomalies in the behavior of CoS, NiS, $Ni(CN)_2$, and $PbMoO_4$. The tentative assumption of a change in constitution—perhaps catalyzed by OH^- ions—presents a fresh point of view, which obviously must remain purely hypothetical until the nature of the supposed change in constitution and chemism of the catalysis are elucidated.

The author believes that consideration should be given to still another explanation for the occurrence of disequilibria and false equilibria. The abnormal resistance of inner complex salts to pH values, at which their precipitation is not possible, corresponds to a more or less persistent passivity. Hence, the term "passive precipitates" seems appropriate for characterizing this anomaly. Such passivity may be the result of an abnormally low tendency by the particles of the precipitate to add and retain water on their surface (hydration). In other words, an hydrophobia is exhibited, which stands in the way of a direct contact with H^+ ions, and also impedes a surface dissociation of the precipitate particles. The reason for the hydrophobia of inner complex salts is, in all likelihood, the fact that in their molecules the metal atoms may be enclosed on all sides by organic radicals that of themselves have no hydrophilic groups and hence possess no centers at which hydration can occur (compare Chapters VIII and IX). There is a relation here to the fact that so many inner complex salts are not readily wetted by water, and also to their frequent solubility in organic liquids. The assumption that hydration is connected with the normal behavior of inner complex salts, and that the lack of hydration is related to a passivity, is supported by observations of the behavior of metal oxinates toward dilute hydrochloric acid.[20a] It is well known that no metal oxinates can be precipitated unless the pH of the solution exceeds a certain value. (With a few exceptions, the lower limit is pH 4.2.) Accordingly, all freshly precipitated metal oxinates should dissolve immediately in 3 N hydrochloric acid, but this is not always the case. The majority of these salts,

[20a] F. FEIGL and G. B. HEISIG, Anal. Chim. Acta 3 (1949) in press.

including those that are known to carry water of crystallization, do dissolve at once in acid of this strength; and likewise, their anhydrous products obtained after drying at 120°C. display no passivity. In contrast, the freshly precipitated oxinates of Al, Fe, Cr, and Ga dissolve just as sluggishly or just as little in hydrochloric acid as the dried products. Especially impressive is the comparison of Al(Ox)$_3$ and Tl(Ox)$_3$·3H$_2$O, which are precipitable in the same pH range. The thallium compound cannot be completely dehydrated even by prolonged drying at 120°C.;[20b] it dissolves immediately in acid. In contrast, when either freshly precipitated or ·dried aluminum oxinate is placed in 3 N hydrochloric acid, the salt remains unaltered at first, and noticeable solution gradually occurs only after about 15 min. The fact that metal oxinates, which carry water of crystallization, show no passivity, even after they are dehydrated, is probably due to their being immediately rehydrated on contact with dilute hydrochloric acid, whereas, the passive metal oxinates dissolve only to the extent corresponding to their lesser hydration capability.

The foregoing discussion deals with a practically unexplored province of the genetic formation of materials. The known cases of solution anomalies come in part from studies not concerned with analytical chemistry. Consequently, little consideration has been given to these abnormalities with respect to reaction specificity and selectivity.

If the solution anomalies that are connected with aging are left out of consideration, the following instances, that were cited in Chapter VI, reveal an indubitable relationship with a tautomerism of the inner complex-former: (1) the precipitation of Cu^{++}, Co^{++}, and Ni^{++} ions with rubeanic acid; (2) the precipitation of Co^{++} and Pd^{++} ions with 1-nitroso-2-naphthol or 2-nitroso-1-naphthol; (3) the precipitation of Co^{++} ions with thioglycolic anilide; (4) the precipitation of Pd^{++} ions with 6-nitroquinoline; (5) the precipitation of K$^+$, Cs$^+$, and Rb$^+$ ions with dipicrylamine. If it is kept in mind that these precipitations involve the aci-forms of the respective precipitants it is possible also to take into account a stabilization of the aci-form in the insoluble salts. A truly extreme case of such stabilization is displayed by Co^{III}-1-nitroso-2-naphthol. This red compound can be precipitated quantitatively only from ammoniacal, neutral, or acetic acid solution but not from strong mineral acid solution. Nevertheless, if once formed, the salt is completely stable toward mineral acids. It can be dissolved in concentrated sulfuric acid, or even in fuming nitric acid, and is reprecipitated from these solutions on dilution.[21]

[20b] Compare F. FEIGL and L. BAUMFELD, *Anal. Chim. Acta* **2**, 416 (1948).

[21] M. ILINSKY and G. v. KNORRE, *Ber.* **18**, 699 (1885).

Reasons other than the development of an active aci-form are the basis of the characteristic behavior of 8-hydroxyquinoline (oxine) toward alkali molybdate and tungstate. Berg[22] states that quantitative precipitations of $(C_9H_6NO)_2MoO_2$ and $(C_9H_6NO)_2WO_2$, respectively, can be obtained only from weak mineral acid or acetic acid-acetate buffered solutions at pH values between 3.5 and 7.6. No precipitate appears from solutions at lower-pH values. On the other hand, these compounds, once they are precipitated, are resistant to subsequent treatment with strong acids, including even concentrated sulfuric acid. This stability is especially true of the molybdenum precipitate. The reason for this remarkable behavior probably is that these oxine compounds, which can be regarded as phenol esters of molybdic and tungstic acid, respectively, are not formed initially. The first products are the salts $(C_9H_7NO)_2 \cdot H_2MoO_4$ and $(C_9H_7NO)_2 \cdot H_2WO_4$, in which oxine functions as a basic cationic constituent. Obviously, these salts are formed only within the stated pH range. After they have been produced, they rapidly undergo inner molecular loss of water and are thus transformed into the acid-stable phenol ester. This transformation can be readily demonstrated in the case of the molybdenum precipitate, since the products produced in the cold and at the boiling point are quite different. If the former is immediately treated with 3 N alkali hydroxide, complete solution occurs almost at once because the oxine molybdate is converted into soluble alkali oxinate and molybdate. In contrast, the product precipitated from a boiling solution is a phenol ester, and hence dissolves but slowly and only when warmed, because the ester must be saponified before solution can occur. The oxine molybdate differs from the oxine ester of molybdic acid also with respect to its behavior toward phosphomolybdic acid and ammonia. Only the former reacts immediately to produce the characteristic blue lower oxides of molybdenum. The rate at which the oxine molybdate goes over into the oxine ester is remarkable. If the precipitate formed in the cold is treated with an excess of hydrochloric acid (1:1), about 66% goes into solution at once; after two minutes 21% will dissolve; after five minutes, 18%; and after 24 hours, not more than 5% will go into solution.[23]

In a few instances, inner complex salts that cannot be precipitated from ammoniacal solution, have been found to be resistant to ammonia. The palladium salts of dimethylglyoxime and 1-nitroso-2-naphthol are pertinent examples. The precipitation does not occur at all, or only very slowly at room temperature when these reagents are added to ammoniacal

[22] R. BERG, op. cit., pp. 64, 65. Compare also G. BALANESCU, Ann. chim. applicata 12, 259 (1930).

[23] F. FEIGL and C. PADRON, unpublished studies.

palladium solutions. The latter contain no Pd^{++} ions, but instead the very stable $[Pd(NH_3)_4]^{++}$ ions. Consequently, these inner complex palladium salts, after precipitation from neutral or weakly acid solution, might be expected to dissolve easily in ammonia water, but they do not. They are resistant not only to ammonia concentrations that prevent the precipitation, but also against far higher concentrations. Hammett and Sottery[24] showed that the inner complex colored salts of aurintricarboxylic acid with aluminum and chromium can be formed only in acetic acid or acetate-buffered solution. Ammoniacal solutions produce precipitates of the respective hydrous oxides only. Here again, it might be expected that ammonia would decompose these solid aluminum or chromium inner complex salts to produce the hydrous oxides. This occurs with the chromium compound, but the aluminum salt is not visibly decomposed. These two compounds of aurintricarboxylic acid have practically the same color but they can be distinguished readily by this divergent behavior toward ammonia.

Hitherto, consideration of the influence of precipitation conditions has been limited almost entirely to the behavior of the precipitates toward acids or ammonia. It can be assumed that these conditions will be reflected also in the behavior of precipitates toward other agents. The interesting findings of Gluud and Schoenfelder[25] substantiate this expectation. They showed that nickel sulfide, precipitated from ammoniacal solutions by ammonium sulfide, behaves quite differently if the precipitation occurs at 9° or 90°C., respectively. The material obtained at the lower temperature produces 83% sulfur and 9.5% thiosulfate ion when air is passed through the ammoniacal suspension, while the sulfide formed at the higher temperature correspondingly yields 8.5% sulfur and 51% thiosulfate ion. An interesting anomalous resistance to CN^- ions has been found in the behavior of palladium oxinate.[25a] This inner complex salt is insoluble in alkali cyanide solutions, even though no precipitation of Pd-oxinate can be obtained from Pd^{++}-KCN solutions, which contain $[Pd(CN)_4]^{--}$ ions. Consequently, a false equilibrium is present, or an equilibrium whose establishment is extremely delayed, for reasons that are as yet unknown. Other palladium salts with α-dioximes and o-hydroxyaldoximes show a normal behavior, in that they are not precipitable from solutions of $[PdCN)_4]^{--}$ ions, and, once they have been precipitated, are dissolved immediately by alkali cyanide.

In the foregoing discussion of the effects of the genetic formation of materials, certain instances were cited in which the production of dense,

[24] L. T. Hammett and C. T. Sottery, *J. Am. Chem. Soc.* **47**, 142 (1925).
[25] W. Gluud and R. Schoenfelder, *Ber.* **57**, 628 (1924).
[25a] F. Feigl and H. E. Feigl, *Analytica Chim. Acta* **3** (1948) in press.

coarse-grained compounds was of analytical importance. However, the purity of the precipitate, as well as its physical characteristics, is important for the purposes of gravimetric analysis. The precipitation conditions necessary to attain both of these ends must be discovered, often by actual trials, which are likely to be tedious in the absence of concrete clues. There are a few general rules that can be followed to obtain pure, coarse-grained precipitates that filter well. Several studies along this line deserve careful consideration. Hahn[26] found that precipitates with these desirable qualities are obtained by "precipitation at extreme dilution." This is accomplished in the case of barium sulfate by allowing solutions of Ba^{++} and SO_4^{--} ions to drip slowly and simultaneously into dilute hydrochloric acid. Another type of precipitation involving extreme dilution of only one of the reactants was used by Chan[27] in precipitating calcium oxalate. No precipitate is formed if Ca^{++} and $C_2O_4^{--}$ ions are brought together in mineral acid solution, but the precipitation does occur in acetic acid or ammoniacal solutions. As a rule, the precipitate thus obtained is very fine and filters poorly. If, however, a solution containing Ca^{++} and $C_2O_4^{--}$ ions and hydrochloric acid is warmed for some time with a large excess of urea, the calcium oxalate separates as a coarse, crystalline, dense precipitate, which settles immediately. The ammonia, or rather the ammonium carbonate, that is gradually produced by the hydrolysis: $CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3$, and which is consumed in the neutralization of H^+ ions, accordingly acts constantly in the state of extreme dilution. The consequence is the precipitation of calcium oxalate in the desirable coarsely crystalline form. Willard and Tang[28] have used the slow rise of pH, occasioned by the hydrolysis of urea in the presence of succinic acid, to obtain a quantitative precipitation (at pH = 4.2–4.6) of aluminum as coarse-grained basic succinate, and to separate it from other metals.

A precipitation at extreme dilution also occurs if solutions of hydrolyzable heavy metal salts are treated with alkali salts of medium strong acids which, under the prevailing conditions, are hydrolyzed to a relatively slight extent. The concentration of OH^- ions is thus constantly kept at a low level, and they are gradually consumed (neutralized) by the H^+ ions provided by the hydrolysis of the heavy metal salt. The

[26] F. L. HAHN, Z. anorg. allgem. Chem. **126**, 257 (1923); see also I. M. KOLTHOFF and M. J. VAN CITTERT, Z. anal. Chem. **63**, 392 (1923).

[27] F. L. CHAN, Dissertation, University of Michigan, 1932, cited by H. H. WILLARD and N. H. FURMAN, Elementary Quantitative Analysis, 3rd Ed., p. 398. New York, 1940.

[28] H. H. WILLARD and W. K. TANG, Ind. Eng. Chem., Anal. Ed. **9**, 357 (1937); see also H. H. WILLARD and H. FREUND, ibid. **18**, 195 (1946).

consequence is that metal hydroxides, which separate in a slimy form when the precipitation is made with ammonium hydroxide, come down in a dense form that filters well. Moser and his associates[29] provided examples. They precipitated $In(OH)_3$ by warming solutions of indium salts with potassium cyanate, and likewise they brought down the hydrous oxides of Fe^{III}, Al, Cr, and Be in the cold by adding ammonium nitrite to the respective salt solutions. Because of their dense structure, the metal hydroxide precipitates produced by these methods have a much lower tendency to adsorb cosolutes than the products resulting from the precipitation with ammonia water.

Hahn and his collaborators[30] found that the production of complex compounds presented a further possibility of employing the principle of precipitation at extreme dilutions. If the ion which is to be precipitated is masked by conversion into a soluble complex compound or complex ion, the original concentration of the ion will be decreased in proportion to the strength of the complex binding or, more exactly, according to the position of the masking equilibrium. If the diminished ion concentration is still just sufficient to react with a precipitant and form a precipitate, the precipitable ions will be replenished from the complex equilibrium. Consequently, the ionic species that is to be precipitated is always present at a reduced concentration, which is dictated by the complex equilibrium or stability constant of the complex ion. Accordingly, the ion concentration conditions are analogous to those prevailing during a precipitation at an extreme dilution that has been produced physically. The principle of precipitating from extreme dilution by converting the ion to be precipitated into a complex is utilized, for instance, when magnesium ammonium phosphate is precipitated from an ammoniacal tartrated magnesium solution. Pure crystalline $MgNH_4PO_4$ is obtained with no coprecipitation of amorphous tertiary magnesium phosphate, which is so frequently the case when the precipitate is brought down from strongly ammoniacal solutions containing no tartrate. The prevention of the coprecipitation of $Mg_3(PO_4)_2$ from the solution of complex magnesium tartrate is explained by the difference in the solubilities of $MgNH_4PO_4$ and $Mg_3(PO_4)_2$. The concentration of Mg^{++} ions in the solution of the complex magnesium tartrate remains low throughout the operation. Consequently, during this precipitation at extreme dilution, practically nothing but the less soluble of the two phosphates, namely $MgNH_4PO_4$, can separate from solution.

A good example of the excellent condition and purity of a material

[29] L. MOSER and F. SIEGMANN, *Monatsh.* **55**, 16 (1930); L. MOSER and F. SINGER, *ibid.* **48**, 673 (1927).

[30] F. L. HAHN, K. VIEWEG and H. MEYER, *Ber.* **60**, 971 (1927).

whose precipitation at extreme dilution is made possible through the production of a complex is provided by ferric oxinate (compare Chapter VI). When this inner complex salt comes down from acetic acid-acetate buffered ferric solutions, it is slimy and hard to·filter. In contrast, the precipitate is dense, filtrable, and quite pure if it is formed from solut ons that contain tartrate or oxalate, *i.e.*, where the iron is present as a complex ferric tartrate or oxalate.[31]

Although there is no considerable body of available material concerning applications of precipitations at extreme dilution, it may be safely assumed that in time this procedure will provide many advantages in gravimetric analysis. The quite varied experiences of the writer have shown that precipitates obtained from solutions containing a not too strong complex-former for the ionic species to be precipitated are always coarser and filter more easily than those obtained from unmasked solutions. The following observation[32] is in line with this constant finding. An oxalic acid solution of antimony and stannic salts contains both of these metals as complex double oxalates. When treated with ammonium carbonate at the boiling temperature, only the tin is precipitated. The $SnO_2 \cdot aq$, which ordinarily is gelatinous, is brought down in an easily filtrable form, because the Sn^{++++} ion concentration (or the hydrolysis) is slight in the oxalated solution. Antimony remains complexly bound and is not precipitated. It is rather remarkable that these two metals in acidic oxalated or phosphated solutions show exactly the reverse behavior as regards the stability of the complexes on treatment with hydrogen sulfide. In this latter case, only the antimony is precipitated as sulfide; the tin remains masked. The following interesting method of determining antimony (and separating it from tin) is an excellent illustration both of the genetic formation of a material, and also of a precipitation at extreme dilution. Vortmann and Metzl[33] found that hydrogen sulfide passed into a hot 'antimonous solution containing much hydrochloric acid plus phosphoric acid does not precipitate the usual orange red slimy Sb_2S_3, but rather a black crystalline modification (stibnite). This precipitation involves extreme dilution both of the Sb^{+++} and S^{--} ions. The concentration of the Sb^{+++} ions is greatly lowered through complex binding of the antimony into $H[SbCl_4]$; the S^{--} ions concentration is lowered through the shift of the equilibrium $H_2S \rightleftharpoons 2H^+ + S^{--}$ in strong acid solution. The result is the deposition of very pure and dense Sb_2S_3. In this way, it is possible to obtain the black modification of

[31] Compare M. NIESSNER, *Z. anal. Chem.* **76**, 135 (1929); H. FISCHER, *Wiss. Veröff. Siemens Konzern* **10**, 1 (1931).

[32] Private communication from A. L. CANTIÇÃO, Rio de Janeiro.

[33] G. VORTMANN and A. METZL, *Z. anal. Chem.* **44**, 525 (1905).

antimony sulfide, which cannot be isolated under normal precipitation conditions.

The conditions attending the preparation of the adsorbents used in chromatography have important effects on their performance. For example, alumina, lime, and magnesia may vary several thousand-fold in their adsorbing capacity, depending primarily on the way in which they have been prepared, activated or deactivated. Hence, it seems that the adsorption ability of compounds can be used as a kind of indicator of the effects of the genetic formation of materials. Doubtless, the surface development of the solid phase plays a great part in every adsorption, but the formation of particularly active centers in the surface surely must also be taken into account. The latter may possibly arise from inhomogeneities incorporated in the adsorbing surface, and have their origin in impurities that enter the product in the course of its formation.

The process for which Kohlschütter proposed the term "genetic formation of material" is the manifested influence of production conditions on the form-species and properties of solid materials. The factors responsible for the determination of these characteristics should obviously be sought in the elementary processes that may operate to varying degrees in the particular reaction medium, either along with, or subsequent to, a producing reaction that can be formulated stoichiometrically. A consideration of the formation of solid products from the reaction of dissolved materials reveals that this is a condensation process proceeding from ionic or molecular dispersion and finally resulting in crystalline or amorphous precipitates. During this condensation, particles with colloidal dimensions arise and, dispersed homogeneously throughout the solution, they form a sol whose life span may be quite varied. The sol form has nothing to do with the crystalline or amorphous structure of the particles. The transition from the sol form into a visible precipitate is coagulation, i.e., a disorderly union into secondary particles that of themselves may be crystalline or amorphous. Sol formation and coagulation constitute a characteristic section in the course of the formation of a precipitate. This period is preceded by two other characteristic processes, namely, the formation and growth of nuclei. The significance of these is clear if it is remembered (see Chapter X) that the solubility of materials (the solubility product in the case of electrolytes) depends on the particle size. Accordingly, for each particle size there is a concentration at which the particles are in a solution equilibrium with the surrounding solution. If particles of a given size come into contact with more dilute solutions they must dissolve. If they meet more concentrated solutions, which are supersaturated with respect to these particles, they must grow. In other words, the particles then act as centers for a

further deposition of the material. Consequently, a further growth to visible forms can occur only on preformed nuclei (crystal growth). In crystalline products, the molecules (or ions) in the nucleus are surely arranged in a fashion which is analogous to that prevailing in a visible crystal. They can be regarded as amicronic crystals. Their growth (crystal development) is now believed to be not a uniform process but, according to modern views, adsorption of dissolved molecules or ions on crystal surfaces occurs first, and this is followed by the proper arrangement of the adsorbate in the particular crystal lattice. Consequently, a crystal habit that deviates from the normal form may arise, or the growth of the crystal may be retarded or even prevented if the nuclei adsorb molecules of foreign cosolutes.[34] An expedient for keeping the surface of a nucleus free is often used with success in preparative chemical operations. It consists in removing the substances that interfere with the crystallization by adsorbing them on active charcoal or other suitable adsorbents.

Both the production of nuclei and their growth proceed at definite velocities that are dependent on the nature of the material, the degree of supersaturation of the solution, the pH, the cosolutes, and still other factors. It is easy to see that these processes will have great influence on the velocity of the development of a new solid phase and its discernibility. It is also clear that the size of the individual crystals is determined by the relation of the rate at which nuclei are formed to the rate at which they grow. If they are formed slowly but grow at a comparatively high velocity, the slow reformation of crystal nuclei falls behind the rapid growth and a comparatively few large crystals result. Conversely, the production of many small crystals will predominate when the nuclei are produced at a high rate but grow slowly. In all probability, the extreme case of a high rate of production of nuclei combined with an exceedingly low rate of growth can be considered as causing the precipitation of an amorphous solid.[35] In this case, there is a confused association of

[34] Compare R. Marc, *Z. Elektrochem.* **20**, 515 (1914); E. Cohen and A. L. Moesveld, *Z. physik. Chem.* **94**, 450, 482 (1920).

[35] According to F. Haber [*Ber.* **55**, 1717 (1922)], the form-species of a precipitate is determined by the relation of the aggregation velocity to the orientation velocity of the primary particles (nuclei). If the former is high and the latter relatively low, amorphous precipitates are formed. If these relations are reversed, crystalline precipitates are produced. In general, the molecules in the primary form of precipitates (crystalline as well as amorphous) have not yet associated themselves into a final form that possesses the least energy and hence is the most stable. The stablest, energy-poorest form is the coarsely crystalline one, that has no structural defects. Consequently, when amorphous forms age, they change into crystalline forms at rates depending on the orientation velocity. Fine crystals, with lattice defects,

nuclei, which in their turn, in contrast to the nuclei of crystalline materials, possess no orderliness in the arrangement of their molecules. Probably the molecules of amorphous nuclei are not so closely spaced as is the case in crystal nuclei, so that it is indeed questionable whether such nuclei should be regarded as separate phases, *i.e.*, as possessing definite boundaries in all directions. As was stated previously, the conditions obtaining in a precipitation reaction have a determining effect on the formation of nuclei, their growth, and also on their aggregation. Form-species and particle size, and also the solubility and color that often are their concomitants, are of significance in the discernibility of a precipitation. It is easy to see that compounds of the same order of insolubility but of different particle size may differ quite distinctly with respect to the ease with which they can be seen. Precipitates of silver chloride and barium sulfate provide an excellent example of this point. Although they have about the same water-solubility, the precipitate of $AgCl$ is far more perceptible than the $BaSO_4$ precipitate, because the particles of the silver chloride are far larger. Hence, the sensitivity of the test for Cl^- (Ag^+) ion is higher than that of the SO_4^{--} (Ba^{++}) test. Differences in particle size, which also manifest themselves in supersaturation phenomena, are responsible for the fact that the discernibility of the precipitation of insoluble compounds does not necessarily parallel their insolubilities.[36]

An important factor attending the production of a solid from solution is that the formation of the nuclei is frequently influenced by substrates on which the nuclei can deposit. This is seen in even the familiar fact that supersaturated solutions are often broken down by invisible dust particles. Consequently, if an indifferent solid is introduced into a reaction theater and, after the solubility product of a compound has been exceeded, nuclei are produced faster on this solid, a "local condensate" will be obtained in place of, or along with, the normal "space condensate." The wall of the reaction vessel sometimes functions as the seat of reaction. This has been observed in reactions between gases as well as in reactions between dissolved materials, *e.g.*, formation of a mirror in the decomposi-

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change into coarse, perfect crystals. While the aggregation velocity is a function particularly of the degree of supersaturation and the absolute quantity of the participants in the reaction, the orientation velocity is, above all, a function of the molecular structure of the compound formed. Highly polar compounds (silver halides, $BaSO_4$, *etc.*) have, as a rule, a high orientation velocity and precipitate directly in the crystalline form. In contrast, among the hydrous oxides of the tri-, quadri-, and quinquevalent metals, because of their less marked polar character, the primary precipitates, and often even the aged preparations, persist in the amorphous condition.

[36] Compare I. M. KOLTHOFF, *Z. anal. Chem.* **86**, 34 (1931).

tion of arsine, or in the reduction of solutions of noble metal salts. Sometimes there is no noticeable difference in the form-species and other properties of the space and local condensate. On the other hand, effects sometimes manifest themselves in the production of local condensates that do not appear when space condensates are formed, and which are reflected also in the form-species and properties of the local condensate. The cases just cited of the formation of mirrors by the deposition of metals on the walls of the reaction vessel are good examples. The possibility that the solid phase introduced into the reaction sphere may not be completely homogeneous must be kept in mind. It may have spots or areas that contain material inhomogeneities (contaminants) or structural differences (surface characteristics, crystal edges, *etc.*). Such inhomogeneities and structural differences are vanishingly few in comparison with the myriads of molecules uniformly dispersed throughout the reaction sphere and hence exert no effect on the latter when there is no direct contact. On the other hand, their number in comparison with the molecules in their immediate neighborhood is far from insignificant. Accordingly, it is clear that certain spots on a solid phase may be decisive in determining the nature of a local condensate. Furthermore, an introduced solid may also function as though it were an apparently indifferent precipitate produced in the reaction sphere. Phenomena of this type were discussed in Chapters IV and V, where numerous instances were given. The latter demonstrate that the material obtained by simultaneous precipitation of two materials may display an entirely different chemical behavior than that exhibited by the components precipitated separately or by a mechanical mixture of these components. Likewise, the paper which serves as the site of spot reactions often exercises an influence on the form-species and reactivity of precipitates, even though it has no direct part in the chemical reaction. This effect is sometimes put to analytical use (see Chapter X). The reaction conditions peculiar to a limited area (*i.e.*, on boundaries) which differ from those in homogeneous spacious reaction theaters, are also prevalent when a solid acts as a direct reactant. This can come about in two ways: (a) the reaction can occur directly on the surface with the molecules or ions that are still part of the lattice; (b) the reaction may involve the dissolved portions of the solid and proceed in its immediate proximity. In both cases, reaction products may result which differ more or less with respect to their rate of formation, as well as form and properties, from the reaction products of the same composition but obtained by another procedure.

The foregoing remarks lead to the conclusion that the site of the reaction also must be included among the genetic factors that may be involved in the production of solid materials. In fact, certain portions

of a reaction theater, mostly interfaces, can acquire a great significance with respect to the realization, and the speed of a reaction, as well as for the permanent or transient retention of the reaction products and their properties. Should this be the case then, adopting Kohlschütter's suggestion, a reaction becomes topochemical (Gr. *topos* = place).

Topochemical reactions are encountered in practically all branches of chemistry. They play a prominent role in many technically important processes, such as corrosion and passivity of metals, galvanizing, flotation, activation and efficacy of bleaching earths, mordant dyeing of textiles, catalyses in heterogeneous systems, chemical reactions of solids in sintering processes, *etc.* In the present connection, particular interest attaches to the manner in which the genetic formation of a material and its often closely related topochemical effects are reflected in analytically important reactions, especially with regard to the specificity, selectivity, and sensitivity of analytical procedures.

Interesting insights into the chemistry of certain types of reaction anomalies can be secured by taking topochemical processes into account. The anomalies that come into consideration here concern facts that have come to light through empirical trials, and many of these curiosities have been known for a long time: (a) Components of coprecipitated products often behave quite differently from mere mixtures. (b) The occurrence of a precipitation reaction causes the precipitation of a second difficultly soluble material, even though the latter when alone is not brought down by the precipitant. The reaction anomaly (b), which is known as "induced precipitation," will be discussed first.

As was pointed out in Chapter V, where relevant instances were cited, an inducing or primary precipitation is distinguished from an induced or secondary precipitation. The extent of the latter event can vary within wide limits according to the nature of the precipitation reaction, the quantity of the reaction partner, and other experimental conditions. If the secondary precipitation does not occur, two different causes may be at work. The first is that the solubility product of the material to be thrown down as the secondary precipitate may not be reached. In the other case, the solubility product is exceeded but no precipitation ensues because of supersaturation. For many years it was assumed that the primary and secondary precipitation proceeded concurrently, *i.e.*, practically at the same time (coprecipitation). Kolthoff[37] demonstrated by a series of studies of induced sulfide precipitations that this is not necessarily true; a secondary precipitation may set in even after completion

[37] I. M. KOLTHOFF and E. PEARSON, *J. Phys. Chem.* **36**, 549 (1932); I. M. KOLTHOFF and R. MOLTZAU, *ibid.* **40**, 779 (1936); I. M. KOLTHOFF and F. S. GRIFFITH, *ibid.* **42**, 531 (1938); *J. Am. Chem. Soc.* **60**, 2036 (1938).

of the corresponding primary precipitation.   He termed this "postprecipi-tation."   The following table is constructed from his measurement of the precipitation of zinc sulfide induced by the precipitation of mercuric sulfide in acid solution.   The data show how the influence of time makes itself evident in the postprecipitation, and also the relatively enormous extents to which an induced precipitation can proceed.

TABLE XXVIII

Postprecipitation of Zinc Sulfide with Mercuric Sulfide
(25 ml. 0.05 M HgCl$_2$, 25 ml. 0.05 M ZnSO$_4$ in 0.035 N H$_2$SO$_4$)

Period of passing in H$_2$S	Period of shaking under H$_2$S pressure before filtering	Per cent total zinc in precipitate
Min.	Min.	
3	0	37.3
4	10	89.2
3	20	91.5
3	60	94.5
3	30	0.1 (without HgCl$_2$)

Kolthoff believes that a postprecipitation can occur only when the postprecipitable compound is already present in its supersaturated solu-tion.   This would signify that, in principle, postprecipitation is a catalytic process, namely, it is the hastening of a normally very slow precipitation from a supersaturated solution.   According to Kolthoff, the process of a postprecipitation from acid solution can be pictured, in the case of sulfides, to be about as follows: The primary finely divided sulfide fixes hydrogen sulfide by adsorption and thus builds up on its surface a far greater concentration of sulfide ion than can be obtained in an aqueous solution with the gas under normal pressure.   If metal ions now come in contact with the H$_2$S (or S^{--} ions) condensed on the surface, a precipita-tion of sulfide occurs in this limited area of contact, even though the sulfide does not come down in the bulk of the solution.   The picture developed by Kolthoff leads to the expectation that every secondary precipitation of this kind will necessarily begin with the primary precipi-tation, because the possibility of adsorbing hydrogen sulfide and of a reaction of the adsorbed H$_2$S exist from the instant the primary precipi-tation starts.   This signifies that, in the strict sense of the word, there is no postprecipitation without some, even though slight, previous copre-cipitation.   Obviously, the extent of the true postprecipitation must

depend on the slowness of the secondary precipitation. Transitions between co- and postprecipitation can be expected according to the speed at which a secondary precipitation proceeds. The author is of the opinion that Kolthoff's view that postprecipitation is merely the breaking up of a supersaturation (with deposition of the postprecipitated sulfide as an independent phase), does not necessarily hold in all cases. Another possible explanation will be advanced later, which can apply to coprecipitation as well as to postprecipitation. For the present it will suffice to point out a very interesting observation by Caldwell and Moyer[38] which is a fine confirmation of the topochemical character of postprecipitation. They showed that the postprecipitation of ZnS following the precipitation of CuS, and of CoS following that of ZnS, can be considerably hindered by adding small amounts (about 1 drop) of aldehydes to the acid precipitation solution. Unsaturated aldehydes of the type R—CH=CH—CHO (especially acrolein and crotonic aldehyde) are particularly effective. It is known that aldehydes, and especially unsaturated aldehydes, react with hydrogen sulfide to produce polymerized thioaldehydes. Accordingly, they concluded that the aldehydes exert this hindering effect because these materials react more rapidly than the postprecipitable ions with the hydrogen sulfide that has been adsorbed and condensed on the surface of CuS or ZnS. As a consequence, the CuS or ZnS surface is covered with a film of thioaldehyde. The production of thioaldehyde and the resulting coating of the surface hinders the further adsorption of hydrogen sulfide and, consequently, also the postprecipitation, or, since both topochemical reactions proceed simultaneously, the extent of the postprecipitation is decreased.

The preceding discussion has dealt with induced sulfide precipitations which involve the breakdown of a supersaturation because of the occurrence of a primary precipitation, or, more correctly, because of the action of products of the primary precipitation. Therefore, this process *per se* sets up the conditions for attaining the solubility product of the secondary precipitate.

As was stated at the start, there is still another kind of induced precipitation in which a precipitation is brought about under conditions at which the solubility product of the secondary precipitate is not reached. Kolthoff designates this case alone as coprecipitation. It becomes clear at once that the product of the secondary precipitation cannot be formed as an independent phase because this would contradict the supposition that the solubility product is not attained. Actually, in this case particles of a primary precipitate bind the molecules of the postprecipitable material in some manner to produce a new unit. The latter,

[38] J. R. CALDWELL and H. V. MOYER, *J. Am. Chem. Soc.* **59**, 90 (1937).

whose solubility product patently must be less than that of the secondary precipitate, may be: (a) a principal valence compound; (b) a stoichiometrically defined complex compound; (c) mixed crystals; (d) a solid solution; or (e) an adsorption compound. The process under discussion is topochemical since the surface of particles of the primary precipitate doubtless serves as the reaction site. Fundamentally, it makes no difference whether these particles are nuclei or particles produced from them by aggregation or coagulation. The speed of the topochemical reaction determines whether it stops at the completion of the primary precipitation with which it begins in any event, or whether it continues for a while longer. In other words, there can be both co- and postprecipitation. It seems an obvious assumption that a topochemical reaction of this kind, which leads to a union (in the broadest sense) with particles of the primary precipitate, can also occur with molecules in a supersaturated solution of a secondary precipitate.

The author's belief that both co- and postprecipitations are the result of topochemical (mostly addition) reactions between the components of primary and secondary precipitates is strengthened by the behavior of sulfides precipitated together but without induction. In such cases, the sequence of the precipitations is determined solely by differences in the solubility products. Far-reaching anomalies in the behavior of the sulfides are often observed in these instances.[39] For example, one of the associated sulfides may lose, to a greater or less extent, its characteristic solubility in acids or alkali sulfide, a fact that cannot be accounted for as being due to a purely mechanical effect (*e.g.*, enveloping of one sulfide by the other). Sometimes it is even possible to obtain such abnormal products by throwing down one of the sulfides and then treating the suspension with a metal salt whose cations combine with the sulfide ions to produce the second sulfide. This procedure represents a *quasi* rapid postprecipitation. Since the same reaction anomalies are observed in such instances, though to a lesser degree, as in coprecipitations, it seems permissible to suppose that the sulfides which take part in the process of forming the new material, for which the author proposed the name "mixed sulfide," react while they are in the colloidal range of dispersion. This assumption is entirely in keeping with the concept that the stablest, energy-poorest form is not necessarily produced immediately when chemical compounds are formed. Rather, forms rich in energy are the initial products, and subsequently these gradually go over into forms possessing less energy. This transition into energy-poorer final forms is the reason for the differences that are so often

[39] Compare F. FEIGL, *Z. anal. Chem.* **65**, 25 (1925); *Z. anorg. allgem. Chem.* **157**, 251, 269 (1926).

observed in the behavior of freshly precipitated products as opposed to those that have aged.

The considerable extent of induction was the thing that first made it possible to demonstrate in certain sulfide precipitations that the total process of induced precipitation can be subdivided into coprecipitation and postprecipitation. However, the phenomenon of induced precipitation is not limited to sulfide precipitations, but occurs, to various extents, in other precipitations. An excellent example was studied by Kolthoff and his associates.[40] They investigated the induced precipitation of zinc, nickel, cobalt, magnesium, and calcium in the precipitation of hydrous ferric oxide by ammonia. These divalent metal ions when alone are not precipitable by ammonia in the presence of ammonium salts. However, if ferric ions are present, considerable induced precipitation occurs, a fact that has long been known. New insights into the topochemical nature of induced precipitations was furnished by the interesting discovery that $Fe_2O_3 \cdot xH_2O$ precipitated at room temperature and then aged in the mixed solution at 98°C., retains various quantities of zinc, nickel, etc., depending on the period of aging. Table XXIX presents some of these findings.

TABLE XXIX

Induced Precipitation of Divalent Metals by $Fe_2O_3 \cdot xH_2O$ Precipitate
(The final metal concentration was 0.02 M, and the supernatant liquid was 0.90 M in ammonia and 0.077 M in ammonium chloride)

Aging period at 98°C.	Induced precipitated metal in per cent				
	Zinc	Nickel	Cobalt	Magnesium	Calcium
Fresh	18.3	14.3	17.4	15.1	12.9
15 minutes	24.1				
30 minutes	....	37	33		
5 hours	35	51	58.5	14.0	4.0
2 days	52.4	....	....	12.1	

These data show that zinc, nickel, and cobalt obviously are subject to coprecipitation and also to extensive postprecipitation. In these cases, the latter cannot be due to the breaking down of supersaturation, since the respective hydroxides are soluble in ammonia with production of ammine salts. Kolthoff ascribes the effect to the formation of ferrites, which accordingly form during the coprecipitation as well as at the post-precipitation. Hence, these examples also demonstrate that the slow

[40] I. M. KOLTHOFF and L. OVERHOLSER, *J. Phys. Chem.* **43**, 767, 909 (1939); I. M. KOLTHOFF and B. MOSKOVITZ, *ibid.* **41**, 629 (1937).

process of postprecipitation can be the result of a chemical reaction of the products of the primary precipitation, since ferrites are principal valence compounds formed by the union of the participating hydroxides with elimination of water. When the precipitates obtained by induced precipitation are aged, they obviously lose their magnesium and especially their calcium. This remarkable fact may be due to a disintegration of the ferrites that are formed initially. However, it is more likely that calcium (magnesium) behaves irregularly because, in contrast to zinc, nickel, and cobalt, it forms no ferrite. Instead $Ca(OH)_2$ is loosely adsorbed and, when the ferric hydroxide ages, the surface is diminished and hence desorption ensues (compare Chapter X). It is quite probable that likewise the hydroxides of zinc, nickel, and cobalt are merely adsorbed in the beginning, and this adsorption constitutes the preliminary stage of the formation of a stable ferrite. This concept is supported by the observation that the contamination of ferric hydroxide by coprecipitated metals is much less when considerable quantities of ammonium salts are present. The reason probably is that the adsorption of ammonium salts leaves less space for the adsorption of the other materials. The topochemical nature of these induced hydroxide precipitations is further shown by the fact that addition of solutions of salts of zinc, nickel, etc., to suspensions of ferric oxyhydrate, freshly precipitated by ammonia, also results in a taking up of the divalent metal by the precipitate. Special attention should be given to the fact, shown in the table, that the metals which enter the $Fe_2O_3 \cdot xH_2O$ precipitate and remain there in considerable amounts are precisely those whose ions combine with ammonia to produce ammine ions and which, in general, are particularly prone to participate in the formation of complexes. Perhaps special chemical effects are thus exhibited in induced precipitations, which are markedly selective in still other particulars. This is evidenced by the finding that the same primary precipitate can occasion secondary precipitations to quite varying extents depending on the associates present in the solution.

A special kind of induced hydroxide precipitation, in which water functions as the donor of OH^- ions, is encountered in mixtures of metal salts that hydrolyze readily. For instance, a titanic salt is quantitatively hydrolyzed to $TiO_2 \cdot aq$ when its acidified solution is diluted and heated to boiling. However, if ferric salts are also present, the titanic oxide always carries down considerable amounts of the iron as can be seen by the yellowish color of the precipitate. This result is obtained even in solutions whose pH is so low that comparable pure ferric solutions deposit no hydrolysis products (hydroxide or basic salt) despite prolonged boiling. The hydroxide precipitation of the iron from the hydrolysis equilibrium of ferric salt solutions is thus induced by the precipitation of

titanic oxide (hydrolysis of titanic salts). This result can be plausibly explained as a binding by the TiO_2 particles of the hydrolysis products of the ferric salt. These products may be basic ferric salts still in true solution or, what is more probable, particles of hydrous ferric oxide that have already reached the colloidal state. In the latter case, the reaction would involve two colloidally dispersed materials (see Chapter X). Other instances of such induced precipitations, in which the reactants are hydrolysis products in the colloidal range, can be cited. For instance, if tin is hydrolytically precipitated as stannic acid in the presence of ferric or other hydrolyzable salts, the hydrolysis products are taken up by the $SnO_2 \cdot aq$. The acceptor, which takes up an hydrolysis product from an hydrolysis equilibrium in an insoluble form, need not itself be an hydrolysis product, such as titanic oxide or stannic acid. Other reactions may lead to a primary precipitate that is capable of carrying down hydrolysis products. Examples are the familiar coprecipitation of ferric iron by barium sulfate, and the quantitative precipitation of antimony, tin, or bismuth by $MnO_2 \cdot aq$ from weakly acid manganous solutions on treatment with potassium permanganate. Here again, the union of $BaSO_4$ or MnO_2 particles with the respective hydrolysis products can be laid in the colloidal stage of the reactants. Still other instances are given in Chapter X.

At first glance, there may perhaps seem to be something unusual about assuming that particles of a precipitate in the presence of the appropriate precipitant (which lowers solubility) can react with a second material, in true or colloidal solution, to form a new, insoluble product. The reverse occurrence, namely, solution of precipitates, is more familiar (HgI_2 in KI, HgS in Na_2S, metal cyanides in KCN, *etc.*). Consequently, it seems fitting here to cite examples which clearly demonstrate that water-insoluble, freshly precipitated compounds can, by addition reactions, be converted quantitatively into stoichiometrically defined insoluble compounds. The addition of alkali oxalate to a lanthanum solution produces initially $La_2(C_2O_4)_3$ and this precipitate then combines with excess alkali oxalate to form $La_2(C_2O_4)_3 \cdot (Alk)_2C_2O_4 \cdot aq$.[41] The action of alkali oxalate with lead chloride (bromide) follows an analogous course. The first product is PbC_2O_4 which, with excess lead halide, then forms $PbC_2O_4 \cdot PbHal_2$.[42] The differences in the various solids obtained in these oxalate precipitations can be established only by analysis. The well-known addition of mercuric chloride (and other soluble mercury salts) to mercuric sulfide to form $HgS \cdot 2HgCl_2$ can be perceived directly, since the color change from black to white is quite apparent. Conse-

[41] I. M. KOLTHOFF and R. ELMQUIST, *J. Am. Chem. Soc.* **53**, 1232 (1931).

[42] Z. KARAOGLONOV and B. SAGORTSCHEV, *Z. anorg. allgem. Chem.* **199**, 7 (1931).

quently, if the reactivity of the particles of a precipitate is great enough so that by their complete transformation they produce particles of a new precipitate and consequently a new phase appears, then certainly there is justification for the supposition that in certain cases such transformations do not proceed to completion and will not lead to the production of a new phase. Under such circumstances the reaction products remain associated with the original primary precipitate. No matter which processes are held responsible for the secondary precipitation, the essential characteristic of the structure of the end-products in induced precipitations may be taken to be about as follows: it consists of a skeleton of the unchanged primary precipitate intimately enclosed by products of the reaction with the secondary precipitate. However, this conforms to the definition of an adsorption. Hence, induced precipitation may also be considered as an adsorption phenomenon which, in fact, it is in many cases.

There are still other kinds of topochemical reactions through which precipitates become contaminated in the same manner as when induced precipitations occur. Certain of these reactions likewise appear to be abnormal and they exhibit even more plainly than induced reactions the close kinship to adsorption. Kolthoff[43] proved that if barium sulfate is shaken with dilute lead perchlorate solution, lead is taken up by the solid in exchange for barium which passes into the solution. From the purely formal standpoint, the reaction can be written: $BaSO_4 + Pb^{++} \rightarrow PbSO_4 + Ba^{++}$. However, this equation should not imply that lead sulfate is produced as a precipitate and as such constitutes a new phase. This is not possible because lead sulfate is more soluble than barium sulfate. The interaction should be interpreted as follows: The reaction takes place on the surface of the solid barium sulfate; barium atoms of the crystal lattice are replaced by lead atoms; there is produced, so to speak, a new compound between Pb-Ba atoms and the sulfate radical. The incorporation of lead atoms in barium sulfate is in keeping with the fact (see p. 101) that coprecipitated $BaSO_4$ and $PbSO_4$ acts only in part as a mixture of these sulfates. For instance, the characteristic ready solubility of lead sulfate in ammonium acetate is lost completely or greatly retarded in the coprecipitated sulfates.

Surface reactions of an analogous kind also take place on other insoluble crystalline materials. Not only the cation but also the anion of the insoluble compound can be exchanged for another cation or anion, respectively. Kolthoff found that, if calcium oxalate is digested with dilute salt solutions, the calcium can be exchanged for manganese or

[43] I. M. KOLTHOFF and E. B. SANDELL, *J. Am. Chem. Soc.* **55**, 2170 (1933); **59**, 1543 (1937); see also I. M. KOLTHOFF and C. A. ROSENBLUM, *ibid.* **55**, 2664 (1933).

barium, and sulfate, iodate, or hydroxyl may exchange with the oxalate group. Accordingly, changes may be brought about by surface reactions of this kind which are not shown by the same reactants in solution. Such surface reactions can be formulated by the following equations, in which the participation of part of the solid surface in the ion exchange is expressed symbolically:

$$\underbrace{(Cat.\ An)_x}_{\text{solid surface}} + cat^+ \rightarrow \underbrace{(Cat.\ An)_{x-1} \cdot (cat.\ An)}_{\text{solid surface}} + Cat^+$$

$$\underbrace{(Cat.\ An)_x}_{} + an^- \rightarrow \underbrace{(Cat.\ An)_{x-1} \cdot (Cat.\ an)}_{} + An^-$$

(Cat, An, cat, an = the exchangeable cations and anions).
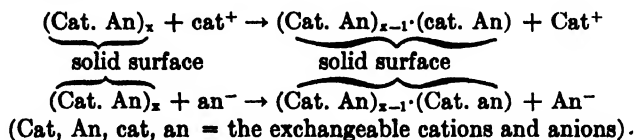
In all exchange reactions of this type there is a union of the cations or anions that have entered the lattice surface with the cations or anions that are resident there. Accordingly, what might be called surface mixed crystals result. If the process of incorporation in the lattice extends into the interior, true mixed crystal formation occurs. The tendency to take up foreign ions in a lattice increases with decreasing solubility of the compound between the assimilated ion and the particular contra-ion of the lattice. A scrutiny of the composition of the products of the foregoing surface reactions reveals an analogy to the products of induced precipitations. These also invariably involve two different cations combined with the same anion, or conversely two different anions and one cation.

This discussion of topochemical reactions on particles of a primary precipitate has thus far taken no account of one factor, namely, the possible contamination of the particles themselves. Under the conditions surrounding an actual analytical precipitation, solutions of a single material never produce a precipitate that conforms absolutely to its stated formula. The particles of the precipitate absorb from the aqueous reaction medium not only water but also the materials dissolved in this medium, i.e., the precipitant which was employed or its dissociation products. In an adsorption on crystalline precipitates there is always preferential adsorption of those ionic species that are present in the lattice. This is manifested in the tendency of the crystal to grow. The extent of an adsorption is especially great among particles in the hydrosol form, which always precedes the production of a visible precipitate. Colloid particles are invariably associated with certain carrier ions, or the latter are adsorbed on the particles of the precipitate and confer sol stability on them (see Chapter X). Coagulation and aging (recrystallization) are accompanied by a diminution of surface because of the production of secondary particles, or of larger or better arranged crystals. Hence, desorption (purging) follows. However, not all of the

adsorbed ions or molecules are given up even then. Consequently, in all stages of the production of a precipitate that forms in the presence of cosolutes, it is necessary to consider not only a reactivity of the particles themselves, which was discussed in the previous paragraphs, but also the exchangeability and reactivity of adsorbed ions or molecules with other ionic species derived from cosolutes. . It is necessary to keep in mind in addition any adsorbed materials that remain in the particles of a precipitate during the growth process.[44]

Topochemical phenomena that lead to the taking up of cosolutes in precipitates may not be disregarded in qualitative and quantitative inorganic analysis. Obviously not more than a minute irreversible accumulation of foreign materials by a precipitate can be tolerated. The specific or selective actions of precipitants, which are always established initially in pure solutions, can be enormously deteriorated by more extensive contamination, which sometimes can even falsify the results. Experience has taught the chemist how to avoid, decrease, or assess the impairment by cosolutes of the action of well established precipitants. On the other hand, it is never possible to predict with certainty whether a new precipitant will produce a pure precipitate when other materials are present. Even those precipitation reactions whose utility has been demonstrated in certain mixed solutions, may prove to be subject to undesirable impairment in other surroundings. Efforts are made to obviate anomalies in precipitation reactions by discovering the conditions under which the extent of disturbing topochemical reactions is as small as possible. Sometimes this can be accomplished quite simply by appropriate modification of pH, by dilution, or by maintaining definite precipitation temperatures. If a precipitate takes up only a portion of foreign ionic species, masking (see Chapter IV) can render excellent service, since the concentration of ions, otherwise causing disturbance, can be lowered by this means. In such cases, purer precipitates can be obtained also by dissolving the precipitate and then reprecipitating it. Sometimes cosolutes that have been adsorbed on the surface of precipitates can be displaced by washing with solutions of materials that are more strongly adsorbed, provided the latter, in turn, can be removed by ignition (ammonium salts, volatile acids, etc.). Perhaps the principle, discovered by Caldwell and Moyer (see p. 636) of preventing or decreasing co- and postprecipitation through the presence of readily adsorbable organic compounds may have possibilities that can be developed.

The incorporation of foreign materials in a precipitate during the

[44] I. M. KOLTHOFF and E. B. SANDELL, Textbook of Quantitative Inorganic Analysis. New York, 1948. Chapter VIII contains examples of the quantitative effects of such processes on the degree of purity of precipitates.

course of its formation is not necessarily a disadvantage. In fact, it may have considerable merit when dealing with traces of material which are so slight that their action with a precipitant is not apparent. Such invisible precipitates can often be taken up by a precipitate produced by the same precipitating agent. By definition this would be an induced precipitation, and the precipitate formed in greater quantities then functions as a trace catcher. Such collection of traces by the particles of a second precipitate is likewise topochemical. A discussion of this phenomenon, which is highly important in trace analysis, was touched on in Chapters V and X. Relevant instances will be given in later portions of the present chapter.

In the topochemical effects that have been discussed thus far the surface of precipitate particles was the seat of reactions with true or colloidally dissolved materials and the reaction products remained in the phase domain of the particles of the precipitate. Such reactions may proceed along two courses: (a) directly with molecules (ions) of the solid particles or (b) through dissolved portions in the immediate vicinity of the surface. In the second case the resultants are fixed on the unchanged surface. There is a widespread belief that reactions of solids with dissolved reactants do not take place with the solid itself, but rather with those portions of it that have gone into solution. When consumed, the latter are constantly resupplied by rapid reestablishment of the solution equilibrium. This mechanism is quite plausible for compounds that rapidly dissolve in water and to a marked extent. However, clear instances are known of direct reactions of solids; the designation topochemical reaction in its strictest sense can properly be applied to these cases also. Prominent in this category is the solution of base metals in aqueous solutions of acids or, in some cases, in alkali hydroxides. Because of the practically complete insolubility of metals in water, there is no doubt that the attack by H^+ or OH^- ions begins on the metal itself with production of metal ions (cations or anions) and discharge of H^+ ions on the metal surface. However, very insoluble binary metal compounds can also interact with dissolved materials without the intervention of the dissolved portions. For instance, mercuric sulfide adds mercuric salts to form insoluble sulfo salts, and it can dissolve in sodium sulfide solutions with production of $Na_2[HgS_2]$. Likewise, mercuric sulfide reacts with aqueous iodine-potassium iodide solutions, producing $K_2[HgI_4]$ and sulfur. This reaction is the basis of an iodometric determination of mercuric sulfide.[45] These reactions of mercuric sulfide cannot proceed *via* dissolved HgS or its ions. The solubility product of

[45] F. FEIGL, *J. Chem. Education* **20**, 176 (1943) discusses the mechanism of this iodometric procedure from the standpoint of a reaction of solid mercuric sulfide.

this salt is 3×10^{-34}, which corresponds to a maximum content of 1×10^{-27} mole HgS/l. Translated, by means of the Loschmidt number, into molecules, this solubility is sufficient to provide only a fractional part of a molecule of HgS per liter, which is a fairly large volume. Accordingly, it is not permissible to count on the existence and activity of dissolved molecules in dealing with these reactions of mercuric sulfide; the locale of the reactions must rather be the solid mercuric sulfide. The same reasoning can be applied to the solution of As_2S_3 and As_2S_5 in alkali sulfides (hydroxides) with production of AsS_3^{---} or AsS_4^{---} ions. The solubility is simply too low, and hence the reactions do not proceed through the dissolved portions of the arsenic sulfides. It must consequently be supposed that the solid arsenic sulfides enter into direct reaction.

Attention is again called to the exchange of bases on silicates and synthetic resins (see p. 518). These instances involve insoluble materials that are electrolytic in nature. In them, by virtue of a reaction that can be formulated stoichiometrically, a cation of the solid electrolyte is exchanged for a cation of the solution without alteration of the solid anionic framework. Consequently, these reactions occur on the surface of a solid and not through their dissolved portions. Finally, it should also be stressed here that many adsorptions are topochemical events, in which molecules of a material that is being adsorbed form addition complexes with molecules of the surface of a solid adsorbent, or react with them.

The high speed of the cited reactions makes it likely that compounds that are more soluble than the extremely insoluble sulfides of arsenic and mercury do not enter into chemical reactions solely through their dissolved portions. Addition reactions and reactions involving exchange of atoms (ions) probably can take place right on the solid free surfaces of difficultly soluble materials. Probably many phenomena of heterogeneous catalysis can be viewed as results of such reactions proceeding directly on the surfaces of solids. In such cases, the solid catalyst may react with one of the soluble reactants to produce an undissolved unstable compound, which, in its turn, reacts rapidly with the second soluble reactant. The solid catalyst is thus regenerated and so plays the same role as a catalytically active soluble compound in homogeneous intermediate reaction catalysis. Examples of heterogeneous catalysis were given in Chapter V, and it is evident that they also can be regarded from the standpoint of being topochemical reactions proceeding on the surface of insoluble catalysts. In this connection, attention can well be directed again to the catalytic acceleration of the sodium azide-iodine reaction by inorganic sulfides (see p. 126). Both soluble

and insoluble sulfides are active in this respect. An homogeneous catalysis is involved when soluble sulfides are present and Raschig[46] made certain assumptions regarding the mechanism in this case. When insoluble sulfides act, the first impulse would be to suppose that the catalysis reaction proceeds through the dissolved sulfide. However, the fact that mercuric sulfide and other quite insoluble naturally occurring sulfides (galena, pyrites, *etc.*) also are active proves that this must be an heterogeneous catalysis. An attempted explanation of the mechanism· of these heterogeneous catalyses was given in Chapter V. It included a topochemical reaction of metal sulfides with free iodine to produce metal iodides.[47] The topochemical reaction of insoluble metal sulfides with iodine and sodium azide provided the first possibility of detecting insoluble sulfides (in the same manner as soluble sulfides) by spot reactions, which are astonishingly simple, but yet specific and exceedingly sensitive.[48]

The postulation of a direct reaction between difficultly soluble solids and materials dissolved in water to form products which then constitute a separate phase, is supported by the behavior of solutions of iodine in organic liquids. It has been found that all heavy metal sulfides can be transformed into their respective iodides by treatment with iodine dissolved in ether, chloroform, carbon disulfide, *etc.*[47] Participation of dissolved portions of the sulfides is definitely excluded in such instances. Golubev[48a] recommended that this method of producing HgI_2 be applied in the systematic scheme of qualitative inorganic analysis for identifying HgS (and Hg-sulfo salts). The reactivity of iodine dissolved in organic liquids (compare Chapter V) was employed by Linhard and Stephan[48b] for an interesting method of identifying silver cyanate. When dissolved in cyclohexene (tetrahydrobenzene) iodine reacts with silver cyanate: $AgCNO + I_2 \rightarrow AgI + CNOI$. The resulting iodocyanate adds to the cyclohexene, with opening of a double bond. The product, which has a characteristic odor, is converted into an insoluble derivative of urea when dry ammonia gas is passed in.

As yet, little consideration has been given to the analytical employment of topochemical reactions of solids with reagents dissolved in organic liquids which are immiscible with water. If it is remembered that many organic inner complex-formers and inner complex salts are readily soluble in such liquids, there is every reason to expect the application in analysis, of topochemical reactions by which inner complex salts are formed.

[46] F. RASCHIG, *Ber.* **48**, 2088 (1915). See also Chapter V.
[47] F. FEIGL, *J. Chem. Education* **20**, 137, 176 (1943).
[48] F. FEIGL, *Z. anal. Chem.* **74**, 369 (1928).
[48a] N. A. GOLUBEV, *Chem. Abstracts* **37**, 4983 (1943).
[48b] M. LINHARD and M. STEPHAN, *Z. anal. Chem.* **88**, 16 (1932).

The following discussion will deal with topochemical reactions of solids with gaseous or dissolved reactants, in which the retention of typical reaction products at the place of their production is of importance to the specificity, selectivity and sensitivity of tests.[49] Topochemical test reactions involving gaseous reactants will be discussed first. Their number is not very large. Among them[50] is the well known Marsh test, in which arsenic hydride is thermally decomposed on a glass surface. Kohlschütter showed that the black variety of arsenic deposited as a mirror on the glass is not an allotropic modification of the element but rather a particular form-species, determined by the substratum. Likewise, the Gutzeit test for arsenic, in which brown-yellow $As(HgCl)_3$ is formed on dry mercuric chloride paper by the action of arsenic hydride, is topochemical in nature. It can be applied even for quantitative determination of small amounts of AsH_3 by comparing the intensities of the colors of the reaction zones formed on the paper.[51] Two tests for the volatilization of mercury at room temperature should be included here, because they too are topochemical reactions of this kind. Nordlander[52] showed that a black fleck is produced when mercury vapor comes in

[49] Mention should be made here of reactions between two solids without intervention of a solvent. These are topochemical in nature, since the site of their occurrence is rigidly localized by the contact of the reactants. Reactions between solids play practically no role in modern methods of analysis. Formerly the Thenard's blue test for aluminum and the Rinmann's green test for zinc were widely used. These mineral colors are Co aluminate and Co zincate; they are produced by the union of CoO and Al_2O_3 or ZnO. The procedure consists in moistening the sample with cobalt nitrate solution and igniting. Studies of the formation of these colored materials were the starting point for the classic work on the reactivity of solids by J. A. Hedvall and his school. His findings are discussed in detail in his "Reaktionsfähigkeit fester Stoffe;" Leipzig, 1939.

F. Feigl, L. I. Miranda and H. A. Suter [J. Chem. Education 21, 18 (1944)] in studies of the reactivity of solids found that oxides of Ti, Zr, Th, Mg, and Be (but not Al_2O_3) when mixed with pulverized, dry lake-formers (alizarin dyes, diphenylcarbazide, etc.) and heated to temperatures below the melting point of the lake-former, produce, within a few minutes, lakes of these various metals, as evidenced by characteristic color changes in the mixtures. The explanation is that heating the lake-former close to its melting point suffices to loosen or distort its molecules enough to permit its rapid adsorption on the solid oxide. Not only lakes but also stoichiometrically defined inner complex salts can be produced by the dry method. Inner complex salts also enter into reactions at temperatures close to their respective melting or sublimation temperatures. Such reactivity of solids must be studied not only for theoretical reasons but because of possible analytical applications.

[50] The gold foil test for mercury, based on the formation of an amalgam, certainly belongs in this category.

[51] W. W. Scott, Standard Methods of Chemical Analysis, 5th Ed., p. 101. New York, 1939.

[52] B. W. Nordlander, Ind. Eng. Chem. 19, 518 (1927).

contact with selenium sulfide paper. The colored products of the reaction: $2Hg° + SeS \rightarrow HgS + HgSe$ are responsible for the fleck. A similar test described by Feigl[53] is easily made. A drop of mercury is placed in a porcelain crucible which is then covered with dry palladium chloride paper. A black ring soon appears on the paper, due to metallic palladium formed by the reaction: $PdCl_2 + Hg° \rightarrow Pd° + HgCl_2$. A modified form of this topochemical reaction can be used to detect mercury by the dry method. It succeeds even with those organic compounds in which this element cannot be detected by the wet method.[53] A well-known topochemical reaction between gaseous and solid reactants is the etching test for fluoride. This is based on the action on glass of gaseous hydrofluoric acid, liberated from fluorides. The glass is etched where it is in contact with the H_2F_2, and is thus rendered less transparent. It was shown by Fetkenheuer[54] that quantities of H_2F_2 which are too small to produce a visible etching of glass nevertheless can bring about another characteristic effect. If a material to be tested for fluoride is warmed in a test tube with a little concentrated sulfuric acid, it will be found that the acid no longer flows uniformly over the walls of the tube when the latter is tilted. Instead, the acid runs together in drops like water on waxed paper. Obviously, the action of the small amounts of H_2F_2 has altered the surface of the glass. Perhaps this action follows an initial adsorption of H_2F_2 on the glass. Possibly, there is also an intermediate production of $SiOF_2$, preceding the liberation of SiF_4.[54a] A specific and sensitive test for cadmium described by Geilmann[55] provides another excellent example of a topochemical reaction with a reactant in the vapor state. If cadmium compounds (oxide, sulfide, carbonate, silicate) are heated with a reducing agent (*e.g.*, sodium oxalate) in a tube closed at one end, the cadmium volatilizes and deposits as a metallic sublimate. This can be converted into yellow cadmium sulfide, which turns red when hot, by subliming sulfur over it. If the ignition tube is charged with about 0.1 g. of the mixture, then drawn out to a capillary, and heated, the sublimate collects in the capillary. As little as 0.002% cadmium can be thus detected in zinc ores and 0.0002% in powdered glass. The action of selenium dioxide on metallic silver is interesting from the standpoint of theory. Water solutions of SeO_2 have no action on metallic silver. If, however, a small heap of SeO_2 is placed on silver foil and heated to 110–120°C. for a few minutes, an adherent black fleck

[53] F. FEIGL, *J. Chem. Education* **22**, 344 (1945).

[54] B. FETKENHEUER, *Chem. Abstracts* **17**, 1398 (1923).

[54a] G. CANNERI and D. COZZI, *Anal. Chim. Acta* **2**, 321 (1948).

[55] W. GEILMANN, *Z. anorg. allgem. Chem.* **115**, 192 (1926); Compare R. BIEWEND, *Berg.-Hüttenmann. Ztg.* **61**, 401 (1902).

forms beneath the unchanged SeO_2.[56] The reason for this topochemical reaction is that SeO_2, which sublimes at 315°C., has enough vapor pressure at the temperature used here to bring about the reaction $2Ag + SeO_2 \rightarrow Ag_2Se + O_2$. The silver selenide formed by the action of SeO_2 vapor remains at the site of its formation. The blackening of silver foil by hydrogen sulfide is analogous to this in principle. A reaction accomplished by the action of a gas on a metallic surface to produce a coherent coating is known as tarnishing.[57]

There are also instances of topochemical reactions between solids and gases or vapors in which a part is played by the volatilization of certain reaction products. A good example is the removal of stannic oxide by heating with ammonium iodide. This result, which was first reported by Moser,[58] is due to the thermal dissociation of the ammonium iodide. The resulting hydrogen iodide is much more active in the gaseous state than in solution. Accordingly, it reacts rapidly with the tin oxide and forms stannic iodide which volatilizes at 340°C.:

$$\text{(a) } NH_4I \rightarrow NH_3 + HI \qquad \text{(b) } SnO_2 + 4HI \rightarrow SnI_4 + 2H_2O$$
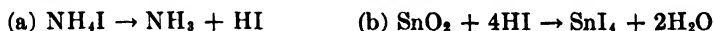
Likewise, arsenic and antimony oxides can be thus converted into the corresponding volatile iodides. Caley and Burford[59] have developed this fuming-off with ammonium iodide into an elegant method for testing the purity of stannic acid. Feigl and Medeiros[60] recently observed that lead compounds, including PbO, PbO_2, $PbSO_4$, and PbS (including native galena), can be quantitatively volatilized by ignition with ammonium iodide. The basic reason is the ease of formation of lead iodide, which boils at 954°C. The foregoing fuming-off reactions involve a seeming paradox in that ignition-resistant compounds are forced to volatilize by being heated with a volatile reagent.

Still other interesting effects are possible through fuming or ignition with ammonium iodide. The thermal dissociation of the latter does not stop with the production of ammonia and hydrogen iodide. Both of them undergo a further thermal dissociation:

$$NH_3 \rightleftharpoons N + 3H \qquad HI \rightleftharpoons H + I$$
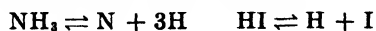
In other words, the heating of ammonium iodide results in the production

[56] F. FEIGL and S. TABAK, unpublished studies.

[57] Tarnishing processes also include the actions of metal surfaces with liquids, and quite generally with electronegative components. The study of the theoretical bases of these tarnishing processes is of rather recent date, but the findings have already shed light on the fundamental processes occurring in the chemical reactions of solid phases, and of the reaction of solids with each other. Compare A. HEDVALL, *op. cit.*

[58] L. MOSER, *Monatsh.* **53**, 39 (1929).

[59] E. R. CALEY and M. G. BURFORD, *Ind. Eng. Chem., Anal. Ed.* **8**, 114 (1936).

[60] F. FEIGL and C. MEDEIROS, unpublished studies.

not only of reactive hydrogen iodide, but also of active (nascent) hydrogen. Consequently, a mixture of alkaline earth sulfate and ammonium iodide when heated undergoes the redox reaction:

$$MeSO_4 + 8H \rightarrow MeS + 4H_2O$$
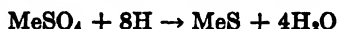
This reduction is followed by conversion of the metal sulfide into the iodide:

$$MeS + 2HI \rightarrow MeI_2 + H_2S$$
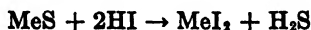
Accordingly, water-insoluble alkaline earth sulfates are quite easily transformed into the corresponding water-soluble iodides by· fuming with ammonium iodide.[61] That these reactions are topochemical and occur on solid surfaces needs no particular emphasis.

The topochemical reactions cited thus far between solid and gaseous reactants, which occur partly in the total absence of water, and partly in the presence of traces of moisture, leave no doubt that the surface of the solid is the site of the reaction. The situation is different when gases react on solids suspended in water or on highly hydrated products. In such cases the same question arises as came up in connection with the reaction of solids with dissolved materials: do the solids react directly or does the reaction proceed between the dissolved portions of the two reactants? Obviously, a decision between these alternatives is of fundamental importance, because reactions of solids can be topochemical, in the strict sense of the term, only when they do not take place *via* solution. An interesting contribution to the unraveling of the way in which solids react is given by the autoxidation of the insoluble hydroxides of Fe^{II}, Mn^{II}, Co^{II}, and Ce^{III} on exposure to the air, *i.e.*, the conversion into higher oxides of these metals, accompanied by characteristic color changes. The autoxidation of $Mn(OH)_2$ to $MnO(OH)_2$ is of special analytical interest. It is the basis of a very selective and sensitive test for manganese with benzidine,[61a] and also of the well known method of quantitatively determining the oxygen content of water.[61b] This manganese test is based on the inclusion of benzidine in the autoxidation process with production of benzidine blue (see p. 332). The basis of the oxygen determination is that all of the oxygen contained in the water is quantitatively consumed for autoxidation when an excess of $Mn(OH)_2$ is present. The resulting Mn^{IV} can then be determined iodometrically. The autoxidation can be represented:

$$2Mn(OH)_2 + O_2 \rightarrow 2\ MnO(OH)_2$$
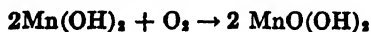
[61] F. Feigl, D. Goldstein and N. Castiel, unpublished studies.
[61a] F. Feigl, *Chem. Ztg.* **44**, 689 (1920); *Z. anal. Chem.* **60**, 24 (1921).
[61b] L. Winkler, *Ber.* **21**, 2843 (1888).

This equation merely presents the stoichiometry of the reaction but tells nothing about the reaction path.   If it is desired to express the fact that the autoxidation proceeds through the reaction of dissolved and constantly reproduced portions of an $Mn(OH)_2$ precipitate, it would be necessary to write:

$$Mn(OH)_2 \rightleftarrows Mn(OH)_2 \rightleftarrows Mn^{++} + 2OH^-$$
$$\text{(solid)} \quad\quad \text{(dissolved)}$$
$$2Mn^{++} + 4OH^- + O_2 \rightarrow 2\ MnO(OH)_2$$
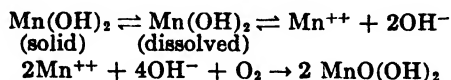
At first sight, this reaction course appears entirely plausible, since the solubility of $Mn(OH)_2$ is relatively considerable (about 0.2 mg./100 ml.). Nevertheless, the author believes that a direct reaction of the solid hydroxide is more probable than a course which involves dissolved portions and dissociation products of the manganous hydroxide.   His reason for this opinion is the fact that manganous carbonate, formed by reaction of manganous salt solutions with ammonium carbonate or guanidine carbonate, or by warming with sodium bicarbonate, is practically unaffected by air, even though the carbonate is about 30 times as soluble as the hydroxide.   Likewise, manganous cinnamate, which gradually precipitates when the highly hydrolyzed solutions of alkali cinnamates are added to manganous solutions, is not autoxidizable.   If the foregoing ionic equation truly represented the autoxidation, the carbonate should behave analogously to the hydroxide, since practically the same conditions prevail, with respect to the concentration of Mn^{++} and OH^- and the presence of oxygen, in an aqueous-alkaline suspension of manganous carbonate as obtain in the case of $Mn(OH)_2$.   Therefore, it seems logical to conclude that the ionic reaction proceeds very slowly, if at all.   This conclusion is in agreement with the familiar fact that molecular oxygen is a sluggish oxidant.   Accordingly, the autoxidation is a specific action of the solid amorphous or finely crystalline $Mn(OH)_2$ and is not produced from the coarser crystalline manganous carbonate.   An explanation of this peculiarity in the behavior of the hydroxide is found in a new concept, which is due to Feitknecht.[61c]   On the basis of interesting studies of the autoxidation of cobaltous hydroxide, he assumes that the first stage in autoxidation consists of an adsorption and the resulting activation of the oxygen.   The adsorption of the molecular oxygen is patently due to the unsaturated character of the oxygen molecule with its double bond.[61d]   If it is assumed that the adsorption of oxygen is an addition adsorption, involving the auxiliary valences of the oxygen atoms of the oxygen molecule, this signifies a loosening (deformation) of the

[61c] W. FEITKNECHT, *Helv. Chim. Acta* **24**, 672, 676, 694 (1941).

[61d] Compare H. WIELAND, L' oxygene, ses reactions chimiques et biologiques. Vieme conseil de chimie, Paris, 1935.

double bond, with consequent approximation of the atomic and, therefore, very reactive oxygen. The divergence in the behavior of manganese hydroxide and carbonate can be fitted into the Feitknecht postulate of an adsorption and adsorption activation of the oxygen. Probably only the hydroxide and not the carbonate is capable of adsorbing oxygen. Since there is no adsorption of oxygen by the carbonate, the activation necessary to the autoxidation does not occur. The writer regards the behavior of manganous hydroxide (and probably other analogous autoxidizable hydroxides) as a nice example of a direct reaction of solids, proceeding without the intervention of dissolved portions. This instance makes it likely that topochemical reactions take place far oftener when solids react than is usually assumed. The behavior of the resulting $MnO(OH)_2$ should also be considered in this examination of the autoxidation of manganous hydroxide. It may separate as an independent phase from the unaltered $Mn(OH)_2$, and then renewed adsorption and activation of oxygen with further production of $MnO(OH)_2$ may follow. However, another mechanism is possible. The weakly acid $MnO(OH)_2$ may react with the basic $Mn(OH)_2$ to form manganous manganite, $Mn(MnO_3)$. This reaction, which is quite likely,[62] may likewise occur as a topochemical reaction.

Solid, difficulty soluble reagents frequently are the basis of exceptionally sensitive tests. They are quite widely employed, principally in the form of reagent papers, in spot test analysis. However, their application is by no means restricted to spot tests. Many years ago, Volhard[63] showed that mercuric oxide functions as a basic precipitant. In 1882, Lecoq de Boisbaudran[64] showed that suspended cuprous or cupric oxide quantitatively precipitate $Ga(OH)_3$ from weakly acid gallium solutions. Since then, solid reagents have been used sparingly, and almost entirely in gravimetric procedures. Among the methods that have been tested recently is the action of "white fusible"—and "white infusible precipitate" on solutions of hydrolyzable metal salts. These reagents, $Hg(NH_3)_2Cl_2$ and $HgNH_2Cl$, respectively, are practically insoluble in water. As Solaja[65] has shown, the action is due to the removal of the H^+ ions produced by the hydrolysis; they are taken up to form NH_4^+ ions. The conditions for precipitation at extreme dilution (see p. 627) are thus provided, and the resulting hydrous metal oxide precipitates filter well.

[62] Compare F. P. TREADWELL and W. T. HALL, Analytical Chemistry, 9th. ed., Vol. 1, p. 220, New York, 1937.

[63] J. VOLHARD, *Ann* **198**, 332 (1879); compare E. F. SMITH and P. HEYL, *Z. anorg. allgem. Chem.* **7**, 82 (1894).

[64] LECOQ DE BOISBAUDRAN, *Compt. rend.* **94**, 1228, 1626 (1882).

[65] P. SOLAJA, *Z. anal. Chem.* **80**, 334 (1930); *Chem. Ztg.* **49**, 337 (1925).

They are easily freed from any excess precipitant by ignition. An interesting fact, that can be applied in analysis, is that the entire phosphate content of a solution containing an excess of aluminum is precipitated as $AlPO_4$ by $Hg(NH_3)_2Cl_2$. Markwood and Mann[66] described a nice example of the applicability of insoluble reagents. They used calomel as a reagent for compounds that furnish OH^- ions. The reaction can be represented:

$$Hg_2Cl_2 + 2OH^- \rightarrow HgO + Hg^° + 2Cl^-$$
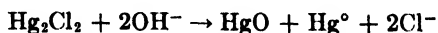
Black free mercury and a soluble chloride result. The latter can be determined titrimetrically in the filtrate. The CaO content of calcium arsenite is an important factor in fixing the value of this insecticide. This determination can be made quickly and elegantly by means of solid Hg_2Cl_2. Feigl and Padron[67] have found that calomel is also an excellent reagent for differentiating normal and basic lead acetate. This is ordinarily a rather difficult assignment. Only the basic salt reacts with Hg_2Cl_2. A good example of modern gravimetric procedures involving the use of a solid organic reagent was provided by Ato.[68] He used camphoric acid as a quite selective precipitant for gallium from weakly acid solutions. He found that the solid acid, which is practically insoluble in water, can be used instead of its alcohol or acetone solutions, or in place of water solutions of its sodium salt. The organic gallium salt is readily converted into Ga_2O_3 by ignition.

The use of organic reagents in the solid form is probably exemplified by all metal precipitations with cupferron from mineral acid solutions. This reagent (see p. 262) is the soluble ammonium salt of water-insoluble nitrosophenylhydroxylamine. The free acid is immediately precipitated when the reagent is added to acidified solutions of metal salts. The acid likewise, and not solely its ammonium salt, is active. This is proved by the fact that acidified cupferron solutions, which therefore contain suspended free nitrosophenylhydroxylamine, react with metal salt solutions in exactly the same way as the ammonium salt. This instance shows that the alkali salts of water-insoluble organic acids that are capable of producing acid-stable insoluble heavy metal salts, can exhibit the same precipitating action as solutions of the free acid in alcohol, acetone, etc. Of course, under such circumstances, the precipitates will not be pure, since free acid invariably will be co-precipitated. However, this can be an advantage in some cases, because the acid functions as collector for

[66] L. N. MARKWOOD and H. D. MANN, *Ind. Eng. Chem.*, *Anal. Ed.* **17,** 570 (1945).
[67] F. FEIGL and C. PADRON, unpublished studies.
[68] S. ATO, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* **12,** 225 (1929); **15,** 289 (1931); **24,** 279 (1934).

small quantities of its metal salt. If these salts are colored, small amounts are rendered far more discernible by such collector action.

The use of solid reagents has been included in the discussion of topochemical reactions, because there is always the possibility that the reactions can begin right on the surface of the solid reagent. Whether this is the only way, or whether the reaction proceeds through the dissolved portions concurrently or exclusively, will be determined by the extent of the solubility and the solution rate of the reagent, and by the velocity of the particular reaction. From the standpoint of the activity of solid reagents, exchange reactions such as were discussed in Chapter X, deserve special attention. It is highly probable that the reaction in such cases does not take place through the dissolved portions of the solid exchanger, but directly on its free surface. Hence, the strictly topochemical nature is quite obvious.

Topochemical reactions between solid and dissolved reactants are of great importance in spot test analysis, where tests on filter paper are carried out in different ways. If drops of the test solution and reagent are brought together on paper, or if a drop of the test solution is placed on paper impregnated with a water-soluble reagent, the capillary spreading of the drops of liquid inevitably produces a dilution, and the reaction products are carried along mechanically. As a result the products spread, or are formed only in certain zones (see p. 576). If, instead, papers impregnated with water-insoluble reagents are used, the reagent has a large surface due to its distribution through the capillaries of the paper, the reaction occurs on the surface of the solid reagent, and the products remain where they are formed. Clarke and Hermance,[69] in a study that is very important for spot test analysis, showed that such topochemical reactions on papers impregnated with insoluble reagents make it possible to secure sensitivities that often are greater by powers of ten than the sensitivities of the same tests made with water-soluble reagents. The following comparison illustrates this point:

Cu-test	with $K_4Fe(CN)_6$	0.5γ Cu
	with $Zn_2Fe(CN)_6$	0.05γ Cu
Cu-test	with Na diethyldithiocarbamate	0.2γ Cu
	with Zn diethyldithiocarbamate	0.002γ Cu
Mo-test	with K ethylxanthate	0.2γ Mo
	with Zn ethylxanthate	0.01γ Mo
Cd-test	with Na_2S	6.3γ Cd
	with ZnS	0.05γ Cd

The preparation of reagent papers by incorporating water-insoluble compounds in filter paper is often closely allied with the genetic formation

[69] B. L. CLARKE and H. W. HERMANCE, *Ind. Eng. Chem., Anal. Ed.* **9**, 292 (1937).

of materials and the occurrence of topochemical reactions. This is especially the case when the reagent in the paper must be produced by a precipitation reaction which takes place in and on the capillaries of the paper. There are various ways of carrying out this operation. Often filter paper is soaked with a salt solution, dried, and then bathed in a solution of the particular precipitant. (If a precipitant can be applied in the gas or vapor state, it is advantageous to fume the paper.) As a rule, it is better not to produce the precipitate all at once, but to deposit it in a series of precipitations. In other words, after bringing down a little of the precipitate, the procedure is repeated. Sometimes it is expedient to impregnate the paper first with another precipitate that adheres well, and then to convert this initial deposit into the desired water-insoluble compound by treating the paper with an appropriate reagent. Temperature and the concentration of the impregnating solutions, the quality of the paper, the method of washing and drying, play important parts in determining the form-species, adherence, and uniform distribution of the material that has been incorporated in the paper. There are no fixed rules for the preparation of reagent papers; the optimum procedure must be determined by trial in each case (see p. 583).

Steigmann[70] developed a novel method of preparing reagent papers impregnated with water-insoluble purely organic salts of water-soluble organic reagents. He found that sapamine (trimethyl-β-oleoaminoethyl ammonium sulfate, $[C_{17}H_{33}\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot N(CH_3)_3]_2SO_4$, forms precipitates with organic reagents possessing strong acidic character (nitroso R salt, chromotropic dioxime, etc.). These insoluble products, after drying, are soluble in organic liquids, chloroform, for instance. If paper is bathed in such solutions, and the solvent allowed to evaporate, the sapamine salt is left as a fine dispersion in the capillaries. When the paper is treated with a drop of a solution that contains a constituent which reacts with the acidic organic reagent, sharply defined flecks are formed. This interesting method of easily preparing stable reagent papers probably will prove quite useful and capable of further development.

Topochemical effects, analogous to those occurring when filter papers impregnated with water-insoluble reagents are used, are encountered in the print method which was introduced by Baumann[71] and Heyn[72] into metallography. It is often employed to detect segregations of sulfur and phosphorus in metallic industrial materials. The principle of this process is that a moist filter paper impregnated with suitable water-soluble reagents, or a silver-free photographic paper, is pressed against a

[70] A. STEIGMANN, *J. Soc. Chem. Ind.* **64**, 88 (1945).
[71] R. BAUMANN, *Metallurgie* **3**, 416 (1906).
[72] E. HEYN, *Stahl u. Eisen* **26**, 8 (1906).

polished section of the metal sample. Typical reaction pictures, that often give definite information concerning the kind and distribution of inhomogeneities, are formed at certain places, *i.e.*, at the site of phosphorus or sulfur segregations, for instance. Niessner,[73] at the author's suggestion, in 1930 began his successful studies to utilize some of the newer reactions of qualitative spot analysis for such local, *i.e.*, strictly topochemical, tests for inhomogeneities in metal sections. If desired, the print can be further developed by immersion in reagent solutions that form other reaction products of greater color contrast or permanence. Shortly thereafter, Gutzeit,[74] in a series of papers, introduced the principle of the printing process into the qualitative examination of minerals and rocks. He likewise used the specific or selective tests of spot analysis. Reference must also be made here to the electrographic methods developed by Glatzunow,[75] and also used by Gutzeit. Glatzunow made the metallic specimen the anode in an electric circuit, with an aluminum foil as cathode. A moist filter paper impregnated with certain reagents, or a silver-free photographic paper, is placed between the electrodes, and serves as electrolyte. When a weak current is sent through the circuit, the specimen is anodically dissolved, and typical reaction products are developed where the reagent paper touches the places at which anodic solution is occurring. Definite tests for metals, metallic coatings, and localization of inhomogeneities can thus be carried out without visible damage to the test object. This process has been used by Hermance[76] for various examinations of metallic surfaces. A remarkable topochemical effect can be observed in the imprint process when testing for inhomogeneities in polished sections of metals or minerals, even though no current is passed. The surface layer of a polished mineral or metal is often more reactive than the original compact material. This is confirmed by the fact that even though certain minerals or metals cannot be visibly etched by a given acid, the same acid will nevertheless dissolve enough of the material to give a print. Possibly, this response may be due to a mechanical loosening in the crystal lattice.[77] It is also possible

[73] M. Niessner, *Mikrochemie* **8**, 121, 339 (1930); **12**, 1 (1932); *Z. angew. Chem.* **52**, 721 (1931); *Berg. hüttenmänn. Jahrb. montan. Hochschule Leoben* **84**, 104 (1936); *Chem. Abstracts* **31**, 978 (1937).

[74] G. Gutzeit, *Trans. Am. Inst. Mining Met. Engrs.* **153**, 286 (1943). This paper contains a list of the publications since 1933 of Gutzeit and his co-workers on the determination and localization of metallic minerals.

[75] A. Glatzunow, *Chimie & industrie* **21**, 425 (1929). A comprehensive presentation is given in *Oesterr. Chem. Ztg.* **40**, 217 (1938).

[76] H. W. Hermance, *Bell Labs. Record* **18**, 269 (1940).

[77] Compare H. Schneiderhöhn and P. Randohr, Lehrbuch der Erzmikroskopie. Berlin, 1934.

that the sectioning and polishing disturb the lattice and so expose active surfaces on which sensitive reagents react more quickly than on compact unpolished areas. It is also probable that plastic deformation which, in fact, corresponds to supplying energy, puts polished areas into a more reactive condition.

A kind of counterpart to the enhanced reactivity of solids at freshly polished surfaces is presented by the greater solubility and reactivity that have often been observed at the surfaces of liquids. It is known that metals which have been partially dipped in corroding liquids, often show more corrosion at the liquid line than in those parts that are completely immersed. Spring[78] was the first to demonstrate, by ingenious experiments, that this phenomenon can be observed with materials other than metals. Examples are calcium carbonate partly immersed in hydrochloric acid, and crystals of sugar, soda, or tartaric acid dipping into water. An explanation has been offered in which it is suggested that the immersed parts of the specimen are protected against dissolution by the downward streaming of the reaction product or its solution. Likewise, atmospheric oxygen may be involved in the increased corrosion of metals at the liquid line. Doubtless many factors are involved and the reasons for the various observed effects may be quite different. However, the studies by Hedges[79] seem to show that the phenomenon can still occur even in the absence of any of the suggested causes. Gurwitsch[80] studied the behavior of organic solids toward organic solvents. He, too, found that the dissolution of solids is more energetic at the liquid line than in the body of the liquids, and that the effect is independent of convection currents of any kind whatsoever. The more rapid solution of solids at the surface of liquids is cited here particularly as an illustration of topochemical effects. However, it is entirely possible that such topochemical effects may also play a part in analytical procedures. Instances include etching tests of polished metal and mineral surfaces, and possibly spot tests on reagent papers. Corrosion pictures on metallic specimens are often the direct subject of analytical examinations, and hence the preferential attack at liquid surfaces can play an important role in such studies. Topochemical analytical reactions on the surfaces of minerals and metals are not limited to the detection of exposed inhomogeneities by the printing and electrographic procedures. Instances are also known in which the surface of a compact metal can function both as the reagent and also as the seat of a test reaction. One of the oldest known cases of this kind is the "hepar test," i.e., the formation of black

[78] W. Spring, Z. physik. Chem. **4**, 658 (1889).

[79] G. S. Hedges, J. Chem. Soc. **1926**, 831.

[80] L. Gurwitsch, Z. physik. Chem. **109**, 375 (1924).

or brown Ag_2S by placing a drop of alkali sulfide solution on silver. An interesting topochemical effect on a metal surface is the test for selenious acid by placing a drop of acidified alkali selenite solution on copper foil.[81] A black fleck of copper selenide is formed on the metal. This test is based on the combined effect of partial reactions, and can be explained as follows. Copper does not dissolve in non-oxidizing acids because the equilibrium $Cu^\circ + 2H^+ \rightleftharpoons Cu^{++} + 2H^\circ$, lies almost entirely to the left. In the presence of selenite, however, the nascent hydrogen is consumed: $H_2SeO_3 + 4H^\circ \rightarrow 3H_2O + Se^\circ$. Thus the selenious acid acts in the same fashion as oxidizing acids, and metallic copper is dissolved. Since these partial reactions occur directly on the surface of the copper, the nascent selenium can react with the copper to form copper selenide. Consequently, if the partial reactions are added (any production of cuprous salts is disregarded) the net reaction on the surface of the copper can be written:

$$3Cu + H_2SeO_3 + 4H^+ \rightarrow CuSe + 2Cu^{++} + 3H_2O$$
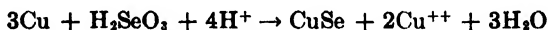
The resulting copper selenide remains at the site of its formation, and forms an adherent black stain when small quantities of selenium are involved.

The following examples of reactions, which can be used for analytical purposes, illustrate the great variety in the mechanisms of topochemical reactions on metallic surfaces. In the course of systematic qualitative analysis, it is common practice to test for antimony by placing a drop of the acidified test solution on platinum foil, and then adding a small piece of zinc.[82] A black coating of metallic antimony forms on the platinum. (If platinum is not used, the antimony deposits on the zinc.) When the test is carried out on platinum, an active local galvanic element is produced. The platinum foil serves as cathode, the less noble zinc as anode, and the drop of the test solution as electrolyte. The production of an electric current thus results in an electrolytic deposition of metallic antimony on the platinum cathode. The mechanism of the "aluminum test for mercury"[83] is often explained in an analogous fashion, namely, as the action of a local element. In this test, a drop of a mercury solution is placed on aluminum foil and an efflorescence known as "sprouted alumina," quickly appears and continues to grow. In view of the remarkable fact that even insoluble mercury salts, such as $HgCrO_4$, HgI_2, or even HgS, bring about this same action when they are rubbed on

[81] Compare TH. W. FRESENIUS, Anleitung zur qualitativen chemischen Analyse, p. 343, Brunswick, 1919.

[82] R. FRESENIUS, *Z. anal. Chem.* **1**, 444 (1862).

[83] The literature on this aluminum test is reviewed by F. CUCUEL, *Mikrochemie* **13**, 323 (1923).

aluminum foil,[84] it is more probable that the mechanism of this catalyzed reaction is as follows: Mercury compounds are reduced by the metallic aluminum to free mercury, which then amalgamates with the aluminum. Amalgamated aluminum is so reactive that it immediately reacts with the oxygen of the air, and with moisture, forming aluminum oxide or hydroxide. Metallic mercury is thus reliberated, again forms the amalgam, and so activates another portion of the aluminum. This alternation continues to repeat itself, and hence this topochemical catalysis reaction can be used as an exceedingly sensitive and specific test for mercury.[85] Mercury exhibits an affinity not only for metals, as shown by the formation of amalgams, but also reacts with many nonmetals. For instance, if chlorine water is shaken with metallic mercury, the topochemical formation of calomel removes all the free chlorine. Any hydrochloric acid present in the chlorine water can then be detected by indicators, or quantitatively determined by a neutralization titration. An analogous topochemical effect can be utilized to reveal traces of sulfur in organic liquids, and traces of hydrogen sulfide in water.[86] The sample is shaken with a drop of mercury, and the mercuric sulfide formed on the surface of the mercury can be detected by applying the sensitive catalytic iodine-azide reaction (see p. 126).

The foregoing test for sulfur or hydrogen sulfide, involving the topochemical formation of mercuric sulfide, is so highly sensitive because the sulfur or hydrogen sulfide originally distributed throughout a large volume is brought to reaction on the surface of the mercury drop, and the reaction product, HgS, is fixed there. The mercury drop thus acts as a *trace catcher* or collector. This type of trace catching, through a topochemical reaction on the surface of a reactant, is also the basis of Pierson's[87] method for detecting minute quantities of gold, platinum, palladium, tellurium, selenium, and arsenic. In this test, very dilute solutions of the salts of these elements are shaken with a little calomel (warming is necessary only in the case of arsenic). Reduction to metallic Au, Pd, Se, *etc.*, occurs on the surface of the Hg_2Cl_2, and is easily perceived because the collector becomes highly colored. As little as 0.05γ Au or Pd and 0.02γ As can be detected in this way, and, if the color intensities are compared, even colorimetric measurements are possible.

These latter instances of collector action are not the only forms in which topochemical reactions are used in trace analysis. In the discussion of induced precipitations in Chapter V, reference was made to the

[84] Compare F. FEIGL, *J. Chem. Education* **21**, 348 (1944).
[85] Compare F. FEIGL, Spot Tests, p. 53.
[86] F. FEIGL and L. WEIDENFELD, *Mikrochemie*, Emich Festschrift, p. 133 (1930).
[87] G. G. PIERSON, *Ind. Eng. Chem., Anal. Ed.* **6**, 437 (1934); **11**, 86 (1939).

fact that the reaction products of inducing precipitations frequently serve as collectors for the reaction products of the induced precipitation. Many induced precipitations doubtless involve typical topochemical reactions (see page 634). Adsorption processes are also topochemical in nature and, if materials are adsorbed quantitatively from very dilute solutions, the action can also be used for purposes of trace analysis. An impressive example of this has been described by Pavelka.[88] He showed that traces of copper can be removed completely from aqueous solutions by shaking the latter with calcium fluoride or talc. The author[89] found that it is possible to detect copper in a solution whose dilution is 1:1,000,-000,000, if 10 ml. of the extremely diluted solution is shaken with a little calcium fluoride, and the latter then assembled by centrifuging. The collector is tested for copper, by means of the Hahn catalysis reaction (see p. 130). Silver can also be detected at great dilutions by trace catching. For example, Ettisch and Tamchyna[90] found traces of silver in 10 ml. of a solution whose dilution was 1:40,000,000. The silver was adsorbed on a colloidal membrane containing protein or glycine, and the spot test with benzylidenerhodanine (see p. 330) was then applied. An ingenious method for trace catching of traces of metals, whose sulfides are less soluble than cadmium sulfide, was described by Clarke and Hermance.[91] A slow stream of the test solution is allowed to run through a little disk of filter paper impregnated with cadmium sulfide. The less soluble sulfide is formed topochemically. After washing, a quantitative determination can be carried out, in some cases through colorimetric comparison with standard flecks. In this way, 1γ copper in 500 ml. of solution can be determined with certainty. The corresponding concentration limit is 1:500,000,000. In another case, as little as 0.0001% copper was determined in "Reinnickel." These examples are sufficient to demonstrate the importance of topochemical reactions in the solution of problems presented by trace analysis.

Typical topochemical reactions occur when solid materials, as fragments or powder, are tested with solutions that have specific or selective actions, when characteristically colored reaction products result. This principle of detection is used frequently in spot test analysis for the identification of rocks and in testing industrial materials. An illustrative example[92] is provided by a reliable method of differentiating calcite and aragonite. It is based on the divergent behavior of these modifications

[88] F. PAVELKA, *Mikrochemie* **23**, 202 (1937).

[89] F. FEIGL, Laboratory Manual, p. 235.

[90] G. ETTISCH and J. TAMCHYNA, *Mikrochemie* **10**, 92 (1931).

[91] B. L. CLARKE and H. W. HERMANCE, *Ind. Eng. Chem., Anal. Ed.* **10**, 591 (1938).

[92] Other examples are given in F. FEIGL, Spot Tests, Chapter VIII.

of calcium carbonate when treated with a solution containing Ag^+ and Mn^{++} ions.[93] This mixture is a sensitive reagent for OH^- ions, with which it produces a black precipitate. The simplified reaction[93a] is:

$$Mn^{++} + 2Ag^+ + 4OH^- \rightarrow MnO_2 + 2Ag° + 2H_2O$$
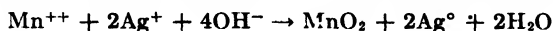
When aragonite is spotted with this reagent solution, it turns black almost immediately. Calcite, in contrast, reacts very slowly. This test is so sensitive that thin sections of stalactites, carrying calcite and aragonite in separate zones, produce a picture resembling a microscopic tissue section, due to the sharply marked tinting of the aragonite zones. The differentiation reaction is based on the differences in the solubility and solution rates of the two varieties of calcium carbonate. The following equilibria are established in both cases:

$$CaCO_3 \rightleftharpoons Ca^{++} + CO_3^{--}$$
$$\text{(solid)}$$
$$CO_3^{--} + H_2O \rightleftharpoons HCO_3^- + OH^- \text{ or } CO_3^{--} + 2H_2O \rightleftharpoons H_2CO_3 + 2OH^-$$
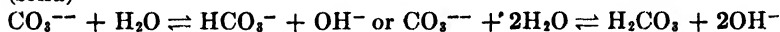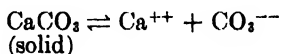
Since aragonite is the more soluble, it furnishes more OH^- ions in a given time than calcite. The OH^- ions react with the reagent solution directly at the site of their production. An adherent deposit of silver and manganese dioxide is thus obtained on the aragonite.

Several model studies will be cited which exhibit interesting details of topochemical reactions of this kind. Feigl and da Silva[94] showed that a "nickel dimethylglyoximate equilibrium solution" is an excellent indicator for all materials which can be considered in the widest sense as being basic, i.e., as consuming H^+ ions. This equilibrium solution is the filtrate obtained after a solution of the nickel salt of a mineral acid has been treated with an excess of dimethylglyoxime. The nickel is incompletely precipitated and the following equilibrium prevails in the filtrate:

$$Ni^{++} + 2DH_2 \rightleftharpoons Ni(DH)_2 + 2H^+$$
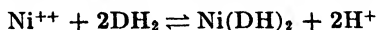
(DH₂ represents a molecule of dimethylglyoxime, and DH its univalent acid radical.) A filtrate of this kind obviously contains all the ionic and molecular species that are necessary to produce a precipitate of Ni-dimethylglyoximate, provided H^+ ions are withdrawn. Accordingly, any interaction with basic compounds is accompanied by a disturbance of this equilibrium and red, water-insoluble Ni dimethylglyoximate precipitates. If, therefore, the equilibrium solution is brought into contact with water-insoluble basic materials, a red precipitate will appear at those places at which H^+ ions are consumed, i.e., on the surface, or in

[93] F. Feigl and H. Leitmeier, Mikrochemie 13, 136 (1933); Mineralog. u. petrog. Mitt. 45, 447 (1934); compare also M. Bray, Chem. Abstracts 40, 4620 (1946).

[93a] See footnote 245 on p. 555.

[94] F. Feigl and C. P. J. da Silva, Ind. Eng. Chem., Anal. Ed. 14, 316 (1942).

its immediate neighborhood.   This reaction is very sensitive because of the striking color and slight solubility of the nickel precipitate, and also because the equilibrium solution is saturated with Ni dimethylglyoximate. If this reagent solution is placed on coarse crystals of magnesite, and similarly on the powdered rock, the powder reacts almost immediately and is colored red, whereas the coarse crystals show no change, even after about 12 hours.   In fact, they do not react with the equilibrium solution, even though boiled with it.   This experiment clearly demonstrates the influence of the grain size, *i.e.*, of the free surface, of a solid on its analytically useful reactivity.   If, when considering the reaction of not too insoluble solids with a reagent solution, it is assumed that only the dissolved portions of the solid react, then the preceeding experiment also shows the effect of the grain size on the solubility of a solid, and on its rate of solution.[95]   The direct reaction of solids, as well as the reaction of their dissolved parts, are obviously of great significance for the initiation of topochemical reactions.   It is remarkable that calcite, both as a powder and in compact pieces, reacts or begins to react almost immediately with Ni dimethylglyoximate equilibrium solution.   This contrasting behavior is the basis of a method of differentiating calcite, magnesite, and dolomite, if tested in large pieces.   The behavior of dolomite is intermediate; it reacts slowly with the equilibrium solution.   When calcite is treated with this reagent, the surface turns pink, then red, and on longer exposure, particularly if shaken, considerable amounts of Ni dimethylglyoximate are detached from the surface.   Many topochemical reactions used in spot tests show a similar reaction picture.   Adherent films of reaction products on the reactive surfaces of solids are obtained, as a rule, only with reactions that proceed slowly, or when very dilute reagent solutions are employed, or in cases in which protective layers are formed (see p. 663).

A very remarkable topochemical effect of its kind is found in the behavior of compact calcite toward a Ni dimethylglyoximate equilibrium solution prepared from nickel sulfate and dimethylglyoxime.   In the cold, this reagent reacts promptly with calcite as just described.   If, however, the experiment is carried out at higher temperatures, then, contrary to all expectation, there is no production of Ni dimethylglyoximate, and the calcite apparently remains unaltered.   The reason for this remarkable behavior is that this particular equilibrium solution contains SO_4^{--} ions, which likewise are topochemically active in the reaction with calcite:

$$Ni^{++} + SO_4^{--} + 2DH_2 + CaCO_3 \rightarrow Ni(DH)_2 + CaSO_4 + H_2O + CO_2$$
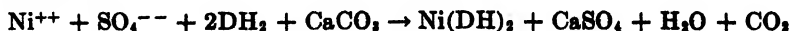
[95] In view of the great difference in the reactivity, an increased energy content due to plastic deformation is conceivable in this case also.

Consequently, calcium sulfate is always formed when an equilibrium solution prepared from nickel sulfate is in contact with calcium carbonate. However, this product is less soluble in hot water than in cold and, furthermore, the reagent solution contains alcohol which decreases the solubility still more. The calcite surface seems to have a great effect on both the rate of nuclear formation of calcium sulfate and on its rate of crystal growth. Probably, calcium sulfate is adsorbed by calcium carbonate, and perhaps is even built into its crystal lattice. The result is that the calcite surface is covered with a layer of calcium sulfate which impedes the penetration of H^+ ions, and thus, under the conditions of the experiment, interferes with the progress of the reaction that gives rise to Ni dimethylglyoximate. As stated, the reaction of calcite with the equilibrium solution containing sulfate is completely inhibited at higher temperatures. Thus, even traces of calcium sulfate are sufficient to produce a perfectly unbroken impermeable·coating. An idea as to the quantities of calcium sulfate required to form this protective layer is obtained if it is remembered that the consumption of even small amounts of OH^- ions suffices to bring about a precipitation of Ni dimethylglyoximate from the equilibrium solution. Consequently, the requisite amount of calcium sulfate must be less than the equivalent quantity of OH^- ions that can be detected by means of the equilibrium solution.

The behavior of calcite toward a Ni dimethylglyoximate equilibrium solution containing SO_4^{--} ions illustrates a very important topochemical effect. It shows that it is possible to so insulate the surface of a reactive material by a coating produced chemically, that the underlying portions are protected against chemical changes. This principle has been applied for a long time in technical chemistry, where it is employed to prevent corrosion. ·On the other hand, protective layer effects received no attention in analytical chemistry. The author, by means of several new tests, has demonstrated that the ulitization of these effects can bring about considerable improvement in specificity, selectivity, and sensitivity. Thus, a specific test for palladium[96] can be made on Ni dimethylglyoximate paper. A drop of the neutral or acetic acid palladium salt solution is allowed to soak in, and then the spotted paper is placed in a dilute mineral acid bath. The Ni dimethylglyoximate of the red reagent paper dissolves, except at the site of the fleck. A red to pink stain is left, depending on the quantity of palladium present. As little as 0.05γ palladium can be distinctly revealed in this way. This procedure involves a protective layer effect which comes about because the acid-soluble Ni dimethylglyoximate dispersed throughout the paper reacts with Pd^{++} ions, and forms acid-insoluble Pd dimethylglyoximate. The

[96] F. Feigl, *Chemistry & Industry* **57**, 1161 (1938).

latter remains where it is formed, *i.e.*, on the suface of the Ni dimethyl-glyoximate, and thus protects the underlying Ni dimethylglyoximate from the subsequent action of the mineral acid.[97] Quantities of palladium that are too small to be revealed by the ordinary dimethylglyoxime reaction on filter paper are sufficient to accomplish this protective action. The great sensitivity of the test is probably due not only to the fact that the Ni dimethylglyoximate reacts directly with Pd^{++} ions, but also to the formation of an analogously constructed palladium salt of the same crystal form. Thus the optimum envelopment of the acid-soluble Ni dimethylglyoximate by the acid-insoluble Pd dimethylglyoximate can result.

Another topochemical protective layer effect is found in a test for sulfur or selenium dissolved in organic liquids. Filter paper impregnated with thallium sulfide is used.[98] If a drop of a solution of one of these elements in carbon disulfide or other organic solvents (*e.g.*, pyridine) is placed on the black reagent paper, and the solvent allowed to evaporate, the sulfur or selenium immediately combines with the finely divided thallium sulfide and forms a polysulfide or selenosulfide. These compounds, in contrast to thallium sulfide, are resistant to mineral acids and hydrogen peroxide. Consequently, if the spotted thallium sulfide paper is placed in dilute acid or hydrogen peroxide, the color is discharged and a red-brown fleck (thallium sulfide) remains. The fleck is due to a layer of thallium polysulfide or selenosulfide that protects the thallium sulfide. This procedure will reveal 3γ sulfur or 1γ selenium in a drop of carbon disulfide or pyridine solution. Technical and pharmaceutical products that have been extracted with carbon disulfide can easily be tested for free sulfur by this method.

Protective layer effects of the foregoing types may be quite generally possible, and may lend themselves to analytical applications, if the product resulting from a spot reaction on a colored reagent paper behaves differently toward chemical agents than the reagent dispersed in the paper. In such cases, especially when the quantity of material to be detected is small, the reaction can occur on the surface of the dispersed reagent. That portion of the reagent which lies below the scene of the reaction may thus be protected against subsequent decolorizing reactions.

[97] F. FEIGL, unpublished studies with C. M. PINTO. They have shown that if $Ni(DH)_2$ is digested with warm neutral $PdCl_2$, the filtrate is practically free of nickel, and only relatively small amounts of palladium are consumed. The residual red $Ni(DH)_2$ is resistant to dilute mineral acids. Obviously, this effect involves an adsorption of Pd^{++} ions or $PdCl_2$ on the surface of $Ni(DH)_2$. If the latter, carrying adsorbed palladium, is treated with acids, a layer of $Pd(DH)_2$ is formed immediately, and it protects the underlying $Ni(DH)_2$ against solution in acids.

[98] F. FEIGL and N. BRAILE, *Chemist-Analyst* **33**, 28 (1944).

For instance, the detection of potassium is more sensitive by the following procedure[99] than by the spot test with sodium dipicrylamine, as usually carried out on a spot plate, or by bringing together drops of the reacting solutions on filter paper. A drop of the solution of the potassium salt is placed on dry sodium dipicrylamine paper. The brown-red paper is then bathed in dilute nitric acid. The color is discharged except for a red fleck that is left where the drop was applied. The potassium salt which is only slightly soluble in water and dilute mineral acids protects the underlying unused sodium salt against solution in the acid. As little as 3γ potassium can be detected in this way, whereas procedures in which there is no possibility of a protective layer effect will reveal not less than 50–100 times this quantity of potassium.

The utilization of a protective layer effect does not absolutely demand that the protective layer be formed by a chemical reaction of the material which is to be shielded, as has been the case in the examples already cited. A second type of protective action is exemplified by the following. Very small quantities of fat, paraffin, or the like, dissolved in easily volatile organic solvents, can be detected[100] by placing a drop of the test solution on paper impregnated with Ni dimethylglyoximate or mercurous chloride. The solvent is allowed to evaporate, and the Ni dimethylglyoximate paper is placed briefly in dilute acid, or the mercurous chloride paper is held over ammonia for a short time. A layer of fat (paraffin) forms on the Ni dimethylglyoximate, or mercurous chloride, and protects the material beneath from solution in acid, or from reaction with ammonia. The result is a red fleck on the Ni dimethylglyoximate paper whose color elsewhere is discharged by the acid. The mercurous chloride paper is turned gray by the ammonia, except where a lighter fleck appears. Here the reaction: $Hg_2Cl_2 + 2NH_3 \rightarrow Hg° + HgClNH_2 + NH_4Cl$ is prevented. These reactions are more sensitive tests for fat than the usual "grease spot test" which depends on the transparency produced on tissue paper by traces of fatty materials. The protective layer procedure described for the detection of fat and paraffin seems to be generally applicable in determining the completion of the extraction of soluble organic compounds by means of low boiling solvents. Studies along this line indicate that materials with a salve-like consistency are more effective than crystalline compounds in forming protective layers. This is understandable, since the surface coatings or protective layers formed by crystalline materials cannot be as continuous as those made up of materials that have a fatty consistency.

The preceding examples of the analytical application of protective

[99] N. S. Poluektoff, *Mikrochemie* **14**, 265 (1933–34).
[100] Compare F. Feigl, Laboratory Manual, p. 88.

layer effects utilized tests carried out on filter paper impregnated with certain reagents.   Another procedure, also involving a protective layer effect, has been developed by Feigl and Pickholz.[101]   They used the water-soluble sodium salt of the osazone of dihydroxytartaric acid for detecting calcium. A light yellow precipitate is formed:

$$C_6H_5-NH-N=C-COONa \qquad\qquad C_6H_5-NH-N=C-COO$$
$$\qquad\qquad\qquad | \qquad\qquad\qquad\qquad + CaCl_2 \rightarrow \qquad\qquad\qquad | \qquad\qquad\qquad Ca + 2NaCl$$
$$C_6H_5-NH-N=C-COONa \qquad\qquad C_6H_5-NH-N=C-COO$$
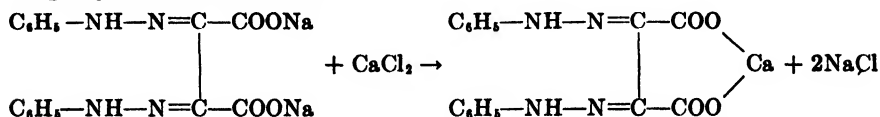
If one or two drops of the saturated solution (1:50) of the reagent is added to 20 ml. of a neutral calcium solution, the presence of calcium is revealed by the development of a turbidity.   The test in this form gives a positive response at a dilution of 1:50,000.   If, instead, 0.1 g. of the solid reagent is added to this same volume (20 ml.) of test solution, the limiting concentration of the test rises to 1:1,000,000.   (The precipitation of calcium as oxalate in the same volume gives positive results, after standing 15 minutes, at a dilution of 1:250,000.)   The explanation of the differences in the sensitivity of the calcium test obtained with the solid or the dissolved reagent, in all probability, is as follows.   The rate of solution of the sodium salt of the osazone of dihydroxytartaric acid in the solution containing Ca^{++} ions is probably lower than the rate at which the insoluble calcium salt is formed.   Consequently, the undissolved reagent becomes enveloped by a layer of the calcium salt, and is thus shielded against rapid and complete solution.   In this way, the calcium is detected by a supplementary protective layer effect, and the sensitivity is about 120 times as great as that attained with the ionic reaction which underlies this method.   In all likelihood, topochemical protective layer effects of this kind will often be found when there are marked differences in the rate of solution of a reagent and the rate at which a new solid phase is produced.   Doubtless, more extensive use will eventually be made of these effects in analytical procedures.

A striking feature of the protective layer effects discussed here is the very wide range of their extents.   This is shown by the quite divergent sensitivities of the tests based on this effect.   In view of the protective layer effect exerted by minimum quantities of calcium sulfate, as described in the case of calcite (see p. 662), it seems fair to ask why a reaction is not invariably checked whenever an insoluble reaction product is deposited on the surface of a material as the result of a chemical change. It is quite clear that even a slight but coherent coating of the surface of a

[101] F. FEIGL and S. PICKHOLZ, unpublished studies; compare also F. FEIGL, Spot Tests, p. 170; compare also HOPKINS and WILLIAMS, LTD., Organic Reagents for Metals. 2nd ed. London, 1934.

reactive solid with an insoluble reaction product could prevent the continuance of the reaction. Experience shows, however, that in the case of filter papers impregnated with insoluble reagents, or when dealing with pulverized samples, *i.e.*, in those instances of topochemical tests of particular interest in spot test analysis, the reactions never cease of their own accord. If such topochemical reactions give rise to colored insoluble products, and if enough of the dissolved reactant is present, intense colorations develop at once, or a color that is weak at the start deepens very rapidly. This same picture of color deepening is encountered in tarnishing processes, and this observation may be taken as evidence that a reaction of this kind occurring on an interface will continue, despite the development of a coating. Finally, it can be shown that adherent films of a reaction product are formed in many surface reactions, whereas, in other cases (often independent of the concentration relations) the reaction products flake off from the free surfaces where they were formed. These differences testify that the production of materials on the free surface of a reactive solid cannot be considered solely as the realization of changes that can be represented stoichiometrically. In fact, partial reactions occur to varying extents, and it is their sum total as well as the physical properties of the reaction product that determine the course and the extent of topochemical reactions.

It is probable that two types of mechanisms, that differ quite considerably, are involved in these topochemical reactions of dissolved reactants, which take place on the surface of reactive solids. The first is the familiar reaction of dissolved materials. This means that aqueous solutions of reagents continuously remove portions from the free surface of the reactive solid phase, and these dissolved portions then diffuse into the water, and, reacting there, produce an insoluble compound. The rate at which nuclei of the newly formed solid phase are formed naturally plays a part here also, as well as whatever influence is exerted by the cosolutes, and perhaps by the solid reactant, on the formation of nuclei and the crystal growth. This mechanism, in which water functions as the carrier of the two reactants, differs fundamentally from the direct reaction of a solid phase. That the latter type of reaction is possible, is shown indubitably by the considerable number of known cases in which solids react in the absence of a solvent,[102] and also by the tarnishing of metals without the presence of a solvent for the particular metal. It is obvious that topochemical reactions of the type of tarnishing processes can occur in the case of those solid phases in which there is no solubility of the solid in the solvent that contains the reagent. A pertinent example is the tinting of cuprous iodide or thiocyanate by alcoholic solutions of

[102] Compare J. A. HEDVALL, *op. cit.* See also footnote 49.

α,α'-dipyridyl and α,α'-phenanthroline (see p. 323). The formation of these colored addition compound with dipyridyl bases proceeds very rapidly, despite the complete insolubility of the cuprous halides in alcohol. An analogous mechanism may apply to other tinting reactions of insoluble compounds and, likewise, to the initiation of the catalytic iodine-azide reaction on the surface of insoluble sulfides (see p. 126).

The processes occurring during the tarnishing of metals have only recently been seriously studied both experimentally and theoretically. It has been shown that even these relatively simplest and clearest cases of the reaction of a solid phase with no solvent present involve very complicated processes. It is certain that tarnishing, and other varieties of reactions of solids, must be separated into definite elementary processes. The primary stage is the real interfacial reaction that always corresponds to a stoichiometric chemical equation. This reaction, which leads to the production of a new solid phase, is followed by the diffusion of both reactants, or parts of them, through the layer of tarnish. However, such diffusion is made possible only by the fact that solids are practically never ideally continuous and free of flaws, *i.e.*, constructed strictly according to the lattice proper to them. There are always defects in their crystal lattices. Such imperfections in "real crystals" (in contrast to "ideal crystals") consist of gaps in the lattice, as well as particles and contaminations that are held in its interstices. It is only this lack of homogeneity that provides a possibility of a diffusion, and therefore, of a continuation of the reactions between solid and solid, solid and gas, and solid and dissolved material. In addition to such diffusion through the interior of solids, and the changes related to this process, there is also the effect of processes leading to the formation of nuclei. These are of considerable importance at the beginning, *i.e.*, when new solid phases are being formed. Accordingly, the reaction velocity of tarnishing processes and, quite generally, of reactions in which solid reactants participate, is determined by boundary reactions, diffusion processes, and the formation and growth of nuclei. The molecular volume of newly formed solid compounds, and their relation to the molecular volume of the solid reactant, appear also to be significant in topochemical reactions. Pilling and Bedworth[103] showed that during tarnishing, protection of the underlying metal occurs only when the molecular volume of the tarnishing compound forming the coating is greater than the atomic volume of the metal beneath it. Probably the extent of protective layer effects that can be used for analytical objectives are connected with such volume relationships.

When two quite different mechanisms are assumed in explaining surface reactions of this kind, it is not necessarily implied that only one

[103] N. B. PILLING and R. E. BEDWORTH, *J. Inst. Metals* **29**, 529 (1923).

or the other of these applied exclusively in any particular case. It is much more likely that both kinds of surface reactions can proceed concurrently, and overlap each other. The extent of the free surface (grain size), the degree of purity of the solid compound and its solubility, as well as the concentration of the dissolved reactant, are important factors.[104]

Regarding the analytical importance of reactions between solids and dissolved substances which lead to insoluble products, a brief reference will again be made to partial processes. Topochemical reactions are involved when surface ions, atoms, or molecules of the solid react directly. The following possibilities should be distinguished in this case. (1) The reaction product initially passes into solution and then precipitates as a separate phase in the immediate vicinity of the reacting surface. (2) The reaction product does not form a separate phase, but remains in the phase association of the solid. This is the case in chemical adsorption (compare Chapter X). (3) The reaction begins on the surface and advances from there into the interior of the solid. Here, as in (1), the reaction product is formed as a separate solid phase; however, it is not absolutely necessary that the contact of the two solid phases be loosened. Finally, reactions can be designated as topochemical if they proceed *via* dissolved and continuously replenished portions of the solid, provided the precipitates are formed in the immediate neighborhood of the surface of the solid and remain there. The velocity of the diffusion processes and the rate of precipitation play a role in determining whether two solid;phases remain together, if one of them is being precipitated from solution.[105]

An excellent illustration of the foregoing discussion is provided by the behavior of palladium cyanide toward ammonia and organic bases. This has so many interesting aspects that the findings pertinent to the present topic will be included here.[106] If amorphous, water-insoluble $Pd(CN)_2$ is warmed with ammonia, crystalline, fairly water-soluble

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[104] In this connection it should be pointed out that conditions which facilitate the start of reactions exist at the edges and corners of crystalline reactive materials. Thus E. PIETSCH, A. KOTAWSKY and G. BEREND Z. *Elektrochem.* **35**, 582 (1929); see also G. M. SCHWAB and E. PIETSCH, Z. *physik. Chem.* **B.1**, 385 (1929) showed that the formation of CuS, and other reactions of metal salts begin on the edges of crystals.

[105] It is beyond the scope of this book to enter further into the theoretical considerations that are of fundamental importance to the kinetics of the reaction of solids. Extensive discussions of these topics will be found in papers by V. KOHLSCHÜTTER that appeared in *Helvetica Chimica Acta, Zeitschrift für Elektrochemie, Annalen der Chemie,* and the *Kolloid-Zeitschrift;* in A. EUCKEN's paper "Energy and Material Exchange at Boundaries," in *Naturwissenschaften* **25**, 209 (1937); in W. JOST's Diffusion und chemische Reaktion in festen Stoffen, Dresden-Leipzig, 1937; and in M. VOLMER's Kinetik der Phasen-bildung, Berlin, 1939.

[106] F. FEIGL and G. B. HEISIG, papers in preparation.

$Pd(CN)_2 \cdot 2NH_3$ results. Probably, ammonia first adds to the solid $Pd(CN)_2$, and the diammine is formed subsequently, through solution and crystallization. Ethylenediamine, α, α'-dipyridyl, and other relatively strong organic bases react in the same way as ammonia. Weak bases do not produce crystalline ammines of $Pd(CN)_2$, but there are formed, depending on the ratio of base: $Pd(CN)_2$, either products of an irreversible adsorption or adsorption compounds. The coordinative linkage between Pd and N atoms, which is the basis of both the formation of the ammines and the adsorption, is so firm that base molecules are fixed on the surface of $Pd(CN)_2$ even from acid solutions. There is an example of hydrolytic adsorption (Chapter X). Neutral and acid solutions of basic dyestuffs react with $Pd(CN)_2$ to form colored adsorption compounds, which can be considered as lakes. Chapter X contained a discussion of colorless and colored adsorption compounds of basic and acidic oxides, in which the organic components were held by principal and auxiliary valences. The adsorption compounds of the neutral $Pd(CN)_2$ are products of a surface-coordination of molecules of base; accordingly, they are representatives of a new class of adsorption compounds. The $Pd(CN)_2$ lakes have essentially the same color as the acid solution of the particular dyestuff.

The behavior of those organic bases which function as acid-base or redox indicators is very interesting. With $Pd(CN)_2$ they form lakes that have the color of the quinoidal form; hydrogen peroxide must be present in the case of the redox indicators. For example, the indicator methyl yellow (p-dimethylaminoazobenzene) is taken up with a red color by $Pd(CN)_2$ from the yellow solutions of the base. Hence, the chemical adsorption brings about the same color change as H^+ ions. This surprising behavior can obviously be explained only by assuming that the acid-base indicators react in quinoidal resonance forms[107] with H^+ ions and solid $Pd(CN)_2$. The color change in the topochemical reaction of $Pd(CN)_2$ with azo indicators makes it possible to impart a characteristic tint to small quantities of $Pd(CN)_2$ and thus identify this compound. The foregoing statements show that topochemical reactions of $Pd(CN)_2$ are not solely of analytical interest, but they also may be of importance with respect to various special fields of chemistry. The functions of the chemistry of specific, selective and special reactions include calling attention to the fact that, by starting with a proposed analytical problem, it is often possible to secure new experimental material, which extends the knowledge of reaction possibilities.

[107] Compare W. F. LUDER and S. ZUFFANTI, Electronic Theory of Acids and Bases, N.Y. 1946, p. 97. See also G. B. BRANCH and M. CALVIN, op. cit., p. 180.

The Analytical Use of Fluorescence Effects and Photochemical Reactions

It has been pointed out in the preceding chapters that the specificity, selectivity, and sensitivity of tests can depend on or be related to a great variety of factors. These include: (a) the normal, or accelerated, or hindered course of chemical reactions; (b) the reaction medium; (c) the manner in which the test is carried out; (d) the problems of complex chemistry; (e) the activity of certain groups in organic reagents; (f) solubility and the ways in which it may be influenced; (g) colloid chemical factors and the effect of free surfaces. Such relationships constitute the body of the chemistry of specific, selective, and sensitive reactions. The present chapter will close this discussion with a consideration of characteristic examples demonstrating the analytical usefulness of fluorescence effects and photoreactions. The employment of these effects and reactions for purposes of analytical chemistry are fairly recent. So many observations concerning the former have been gathered in these comparatively few years, that it has become common practice to refer to this extensive field of application as fluorescence analysis, or sometimes as luminescence analysis. Photoreactions, *i.e.*, reactions that may be affected by light, are much less accessible for analytical purposes than fluorescence effects, and consequently they have been accorded much less attention. Nevertheless, enough has already been discovered to make it safe to predict that many useful items will be found among the numerous chemical reactions that can be influenced by the action of light.

In fluorescence analysis, the object under investigation is finally observed while it is being irradiated under ultraviolet light with a wavelength of 300 to 400 mμ. Various types of "analytical quartz lamps" are used as sources of suitable light. Numerous materials, under these conditions, are incited to emit light of long wave lengths, and then glow in colors that are often characteristic and intense. This emission is known as *fluorescence*. Frequently, a fluorescence can be observed even in daylight or under artificial illumination, because rays of the visible as well as the invisible part of the spectrum can incite fluorescence. However, only the blue and violet, especially the ultraviolet, rays are capable of producing striking fluorescence phenomena. Since light sources, such as the quartz lamp, that are rich in ultraviolet always emit a great deal of white light also, it is necessary to remove the latter by suitable filters. It can be taken as a rule that a slight fluorescence, hardly visible in day-

light, becomes quite distinct if the observation is made under filtered ultraviolet light.

The examination of the characteristic colors appearing in ultraviolet light has proved a very valuable method for distinguishing many preparations. H. Lehmann was the first (1910) to point out this possibility. Shortly afterwards, R. Wasicky used fluorescence analysis to characterize and identify pharmaceutical products. This field has since been developed in the most varied way, particularly by P. W. Danckwortt, M. Haitinger, and H. Neugebauer.

Fluorescence phenomena have been observed preponderantly with organic compounds and applied in their analysis, but characteristic cases also occur with inorganic compounds. For instance, numerous uranium salts exhibit a specific yellow-green fluorescence, and zinc oxide fluoresces in various colors.[1] Even extremely minute traces of mercurous chloride can be detected by its orange-red fluorescence. This test is so delicate that a positive result is given if a drop of mercury has run over mercuric chloride.[2] The quantity of Hg_2Cl_2 formed in this way is so minute that it is not revealed by the familiar reaction, in which free mercury is produced by the action of ammonia on calomel:

$$Hg_2Cl_2 + 2NH_3 \rightarrow Hg° + NH_4Cl + HgNH_2Cl[3]$$
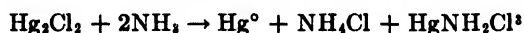
According to King,[4] if the mercuric chloride paper used in the Gutzeit test is viewed in ultraviolet light, quantities of arsenic, which forms $As(HgCl)_3$, that are invisible in ordinary light can be detected. Fairhail and Prodan[5] found that finely divided yellow cadmium sulfide gives a strong yellow fluorescence in ultraviolet light; for example, an inconclusive turbidity of cadmium sulfide (10γ Cd in 50 ml.) can be definitely detected by its fluorescence. Borax beads are very useful in macroanalysis for the recognition of rare earths; some of them not only have characteristic fluorescence colors but also exhibit well-developed fluorescence spectra.[6] A thorough examination of a large number of pure inorganic preparations showed that none of them (with the exception of the well-

[1] Compare E. Beutel and A. Kutzelnigg, Monatsh. 61, 69 (1932).

[2] O. Wolf, Chem. Ztg. 36, 197, 1039 (1912).

[3] Many books on inorganic and analytical chemistry contain no reference to the work of F. Feigl and A. Sucharipa [Z. anal. Chem. 67, 134 (1926)] on the calomel reaction. They found that this does not proceed directly as shown in the equation given. Black mercuroamido chloride, Hg_2NH_2Cl, is formed first. This then decomposes into Hg and $HgNH_2Cl$. Compare E. Gleditch and T. E. Egidius, Z. anorg. allgem. Chem. 226, 265 (1936); Compt. rend. 202, 574 (1936).

[4] A. King, J. Soc. Chem. Ind. Japan 47, 301 (1928).

[5] L. Fairhail and L. Prodan, J. Am. Chem. Soc. 53, 1321 (1931).

[6] Compare M. Haitinger, Akad. Wiss. Wien (Abtlg. IIa) 142, 339 (1933).

known fluorescing uranium compounds) can be used directly for analytical purposes.[7] The conditions are quite different among inorganic natural products, minerals in particular. Many species of these display such pronounced fluorescence that this property can be used directly to characterize such minerals or to determine their origin.[8] In practically all cases, the fluorescence of minerals is due to a content of foreign metallic constituents incorporated in the crystal lattice. Special attention should be given to the behavior of scheelite ($CaWO_4$) and powellite ($CaMoO_4$), which fluoresce intensely (blue and yellow, respectively). The fluorescence colors of natural scheelites, which almost always contain molybdenum, range widely from blue through white to yellow. Cannon[9] concluded that there must be a relation between the fluorescence colors and the respective molybdenum contents. Trials with prepared mixtures of synthetic $CaWO_4$ and $CaMoO_4$ showed that the bright blue fluorescence of $CaWO_4$ passes through light blue to white on the addition of up to 0.5% of molybdenum. From this amount up to 4.8%, the fluorescence becomes increasingly yellow, and from 4.8% upward is identical with the fluorescence color of pure $CaMoO_4$. A surprisingly accurate method for determining the molybdenum content (up to 4%) of scheelite was developed on the basis of the change in fluorescence color being proportional to the molybdenum content. The fluorescence color of the powdered mineral specimen is compared with the colors displayed by irradiated mixtures of known molybdenum content. This is the single known example in which a change of fluorescence color by an accompanying material has been usefully employed in fluorescence analysis. Usually, changes in fluorescence colors due to accompanying materials are undesirable effects, which may seriously impair the certainty of fluorescence tests.

Purely inorganic compounds, produced in the course of analytical procedures, seldom display a characteristic fluorescence. Consequently it seems logical that metal compounds with characteristic fluorescent properties should be sought principally among normal salts and complex compounds with organic components. Pertinent studies with analytical objectives were not made until rather recently, i.e., not until organic reagents acquired more attention. The first observations of daylight

[7] M. HAITINGER, F. FEIGL and A. SIMON, *Mikrochemie* 19, 117 (1931).

[8] A list of fluorescing minerals, together with references to the pertinent literature, is given in J. DE MENT, Fluorochemistry, New York, 1945, pp. 429–497. See also O. C. SMITH, Identification and Qualitative Chemical Analysis of Minerals, New York, 1946.

[9] R. S. CANNON, JR., *Eng. Mining J.* 143, 65 (1942); U. S. Patent 2,346,661; *Chem. Abstracts* 22, 5754 (1944).

fluorescence accompanying the formation of insoluble organic metal compounds were made, however, 80 years ago. Goppelsroeder[10] discovered the yellow-green fluorescence produced at the reaction of morin and aluminum salts, and Jaffe[11] noted that a green fluorescence is obtained by the action of zinc salts with urobilin, the bile pigment. The chemistry of the latter reaction has not yet been elucidated. The extremely sensitive morin reaction (identification limit 0.0001γ Al) is due, according to Schantl[12] to the production of an inner complex aluminum salt of morin (3,5,7,2′,4′-pentahydroxyflavone) or a hydrosol of this salt. Zermatten[13] and Beck[14] showed that Be, Ga, Sc, and In likewise form fluorescing morin compounds. They developed tests for these metals on this basis.[15] The fluorescence of oxine (see p. 181), which by itself does not fluoresce in either acid or alkaline solutions, has been emphasized by various authors.[16] Goto,[17] who has worked extensively with analytically useful fluorescence reactions, described sensitive fluorescence tests for Al, Cd, Zn, Be, Zr, and Ca, based on the not too selective production of the respective metal oxinates (compare Chapter VI). It is remarkable that not all inner complex metal oxinates of colorless metal ions fluoresce; perhaps this is related to the fact that metal oxinates can appear in two isomeric forms (compare Chapter VI). Velluz and Pesez[18] developed an interesting procedure for the detection of ammonia and organic bases which are volatile with steam; its basis is the use of filter paper impregnated with oxine-containing zinc sulfate solution, which produces an intensely yellow fluorescing zinc oxinate on contact with these bases. They claim that this test for ammonia is about five times as sensitive as litmus paper.

Sandell,[19] by means of gallium oxinate, was the first to show that the solubility of inner complex oxinates in chloroform, and the fluorescence

[10] F. GOPPELSROEDER, Z. anal. Chem. **7**, 195 (1868).

[11] M. JAFFE, Virchow's Arch. path. Anat. **47**, 405 (1869).

[12] E. SCHANTL, Mikrochemie **2**, 174 (1924).

[13] H. ZERMATTEN and J. VERSLUYS, Proc. Acad. Sci. Amsterdam **36**, 868 (1933); Chem. Abstracts **28**, 1953 (1934); compare also E. B. SANDELL, Ind. Eng. Chem., Anal. Ed. **12**, 762 (1940).

[14] G. BECK, Mikrochemie **20**, 194 (1936); Mikrochem. Acta **2**, 9, 287 (1937).

[15] Regarding fluorescence reactions of morin with other metals compare H. GOTO, Chem. Abstracts **32**, 5721 (1938); **35**, 1720 (1941).

[16] Compare P. DANCKWORT, Luminescenzanalyse im filtrierten ultravioletten Licht, 3rd. ed., Leipzig, 1934; E. BEUTEL and A. KUTZELNIGG, Monatsh. **55**, 158 (1930); J. EISENBRAND, Pharm. Ztg. **75**, 1033 (1930).

[17] H. GOTO, Chem. Abstracts **35**, 1720 (1941).

[18] L. VELLUZ and M. PESEZ, Chem. Abstracts **41**, 1175 (1946).

[19] E. B. SANDELL, Ind. Eng. Chem., Anal. Ed. **13**, 844 (1941).

of these solutions, can be employed for quantitative purposes. Moeller[20] described colorimetric determinations based on spectrophotometric measurements of chloroform solutions of metal oxinates. He showed that the pH values required for the extraction of oxinates of Fe, Cu, In, Bi, Al, Ni, and Co are partly identical and partly higher than the pH values necessary for the precipitation of the respective oxinates.[21] Consequently, it is noteworthy that Sandell found that gallium oxinate, which can be quantitatively precipitated at pH 6–8, can be quantitatively extracted from an aqueous solution, with a pH as great as 2.3–3, by shaking with chloroform. In explaining the apparent irregular behavior of gallium oxinate, it must be kept in mind that the non-occurrence of precipitation below a certain pH value is not equivalent to a complete lack of reactivity (compare Chapters II and XI). Every precipitation begins before the precipitate becomes visible; however, it may proceed to such slight extents that the solubility product is not reached, or else is not exceeded. In the case of the extraction of gallium oxinate at pH 2, traces of the formed and molecularly dissolved gallium oxinate enter the chloroform. The equilibrium in the aqueous solution: $Ga^{+++} + 3HOx \rightleftharpoons Ga(Ox)_3 + 3H^+$ is thus constantly losing gallium oxinate, and the process continues until practically all of the gallium present has reacted. The Sandell procedure thus demonstrates a fundamental possibility: reactions which do not proceed to more than a slight extent in water solution below a certain pH value, can be carried to an analytically useful point by shaking the aqueous reaction mixture with an immiscible solvent. A necessary assumption is that the partition equilibrium of the reaction product between the water and the immiscible solvent be greatly in favor of the latter. Such equilibrium shifts can raise the selectivity of reactions, as is the case with gallium oxinate, which, without extraction, can be brought down only in a pH interval within which other oxinates likewise precipitate.[22]

The following observations concerning fluorescence reactions of oxine are included here not only because they deal with analytically interesting effects, but also because they provide interesting insights into the field of the chemical adsorption of dyes. Bright yellow aluminum oxinate

[20] TH. MOELLER, *Ind. Eng. Chem., Anal. Ed.* **15,** 270, 346 (1943).

[21] Concerning pH intervals for the quantitative precipitation of metal oxinates compare I. M. KOLTHOFF and E. B. SANDELL, Textbook of Quantitative Inorganic Analysis, p. 80, New York, 1943.

[22] F. FEIGL (unpublished studies) has observed that a case of this kind is found in the vanadium-oxine reaction. An acidified vanadate solution containing oxine shows no sign of a reaction. When shaken with chloroform or amyl alcohol and the layers allowed to separate, the organic layer will be greenish. This indicates the formation of $V_2O_5(C_9H_6NO)_4$.

fluoresces intensely yellow-green, and dissolves in chloroform with a yellow color and retention of the fluorescence. The limit of visibility of the yellow color is reached in 0.001% solutions, whereas the fluorescence can still be seen in 0.000001% solutions. This is an indication of the analytically important fact that fluorescence colors can be much more visible than daylight colors, and furthermore that the fluorescence is not connected with the solid state of the aluminum oxinate, but is also a property of the molecularly dissolved salt. If a chloroform solution of oxine is shaken with alumina, the fluorescing filtrate, depending on the oxine concentration, is either yellow or colorless, which shows the formation of dissolved aluminum oxinate. However, the filter residue, which displays no change in daylight, likewise is fluorescent, and retains this characteristic even after prolonged washing with chloroform. If a highly diluted (*ca.* 0.0003%) solution of oxine is used, the filtrate is colorless and non-fluorescing, while the residue is strongly fluorescent. The same behavior is shown by solutions of oxine in alcohol, water, and ammonia water. Since the fluorescence is due to the inner complex binding of the oxine with aluminum, it may be assumed that a surface reaction has occurred between the alumina and the oxine, which leads to an inner complex binding of the oxine to aluminum atoms without formation of aluminum oxinate as a separate phase. This conception is substantiated by the fact that water solutions of sulfonic acids of hydroxyquinoline (7-sulfo-8-hydroxyquinoline and 7-iodo-5-sulfo-8-hydroxyquinoline), which give no precipitates with aluminum ions, likewise cause alumina to fluoresce. Since the sulfonic acids possess the same inner complex-forming group as the parent compound, oxine, their fluorescence reaction with alumina is a fine example of the fact that fluorescence depends on group action. The foregoing fluorescence reactions are plain examples of the type of surface reactions which have been assumed to be essential for the dyestuff reactions leading to the formation of lakes.[23]

In conformity with the fact, previously mentioned, that exceedingly dilute solutions of aluminum oxinate fluoresce, is the finding that the adsorption of minute quantities of oxine on alumina can be detected through the concomitant fluorescence. It was found that 0.05γ oxine dissolved in 500 ml chloroform, *etc.*, after shaking with 0.2 g. alumina, will cause the latter to fluoresce. This corresponds to a collector action at a dilution of 1:100,000,000,000, which doubtless is a record.

New analytical applications of fluorescence reactions of oxine have been studied.[24] It has been found that yellow fluorescing flecks result when paper is spotted with dilute solutions of oxine, if the paper contains

[23] F. FEIGL and H. W. ZOCHER, paper in preparation.
[24] F. FEIGL and G. B. HEISIG, *Anal. Chim. Acta* **3** (1949), in press.

Ca, Mg, or Al. Qualitative and quantitative filter paper can readily be distinguished in this manner. If qualitative paper, which has been brought to fluorescence by oxine, is brought into contact with gaseous hydrogen fluoride, the fluorescence is quenched because of the formation of the corresponding metal fluoride. The same extinction is obtained with quantitative filter paper, which was impregnated with aluminum oxinate.

The fluorescence reactions, just discussed, of morin, oxine, and oxine derivatives, have high sensitivity but low selectivity. White and Lowe[25] discovered an organic compound, which makes possible a fluorescence reaction that is not only sensitive but also specific. It is the acid azo dye, 4-sulfo-2-hydroxynaphthaleneazonaphthol(I). An acetic acid solution of this dye, which has the trade name Pontochrome Blue Black R, reacts solely with aluminum to produce an orange-red fluorescence, which permits the detection of aluminum at a dilution of 1:5,000,000. The formula (I) shows that the dye contains acid OH groups in such spatial relation to coordinatable nitrogen atoms, that the inner complex salts shown in (II) or (III) can form.
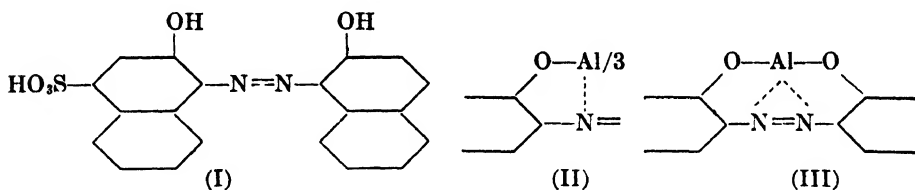
It has not yet been proved whether inner complex salts are actually present in the fluorescing solution. Possibly the dye reacts with sol particles of hydrolysis products of the aluminum in the manner of lake-forming dyes, and a fluorescing lake is produced in the fluorescence reaction. It is quite remarkable that other metals, which are capable of forming inner complex salts and lakes, do not react with this dye. Fluoride ions interfere with the test because of the formation of complex $[AlF_6]^{---}$ ions; accordingly, the fluorescence is quenched on addition of fluoride. This makes possible a method of detecting fluoride. It is interesting, according to Radley,[26] that the dye, 4-sulfo-2-hydroxy-α-naphthyleneazo-α-naphthalene, which is known as Solochrome Black 6 BFA, and which is isomeric with (I), reacts with aluminum as well as with gallium to produce a blood red fluorescence. As a spot reaction, this will reveal 0.1γ Al or Ga. It is probable that in Solochrome Black,

[25] C. E. WHITE and C. S. LOWE, *Ind. Eng. Chem., Anal. Ed.* 9, 430 (1937); compare also M. BORNSTYN, *Bull. soc. chim. France* [5] 8, 540 (1941).

[26] J. A. RADLEY, *Analyst* 68, 365 (1943).

the diazo group attaches not in the *ortho* but in the *para* position relative to the OH group of the α-naphthol, so that inner complex binding is possible only as shown in (II) but not as shown in (III).   In any case, the divergent behavior of the isomeric dyes shows that certain groups are significant for the production of a selective fluorescence attending salt formation.

Even if, according to the foregoing, inner complex binding can be the cause of the fluorescence of metal salts, it is not permissible to regard it as the sole requirement.   An organic compound, which either fluoresces of itself, or is capable of fluorescence in inner complex binding, can lose the fluorescence through binding to quenching metal atoms.   This is shown by the fact that the oxinates of Fe, Cu, Tl,[III] and Ti, which are certainly inner complex salts, do not fluoresce.   Furthermore, Goto (*loc. cit.*) found that the strong fluorescence of salicylic acid and its alkali salts disappears when it is converted into its iron, nickel, or titanium salts, which are inner complex in character.   Doubtless, the appearance and disappearance of fluorescence, as well as color, is connected with structural changes.

Among dissolved compounds, there is often a dependence of the fluorescence on the prevailing pH, in analogy to acid-base color indicators, whose color is also related to pH.   Krueger[27] was the first to point out that the fluorescence of a water solution of fluorescein disappears when traces of acid are added, and is restored on alkalization.   He used this effect in acid-base titrations.   Stark[28] was the first to show that 2-methyl-3-aminoquinoline in water solution exhibits no fluorescence, whereas salts of this base have a distinct blue fluorescence, which disappears again on alkalization.   The use of the so-called fluorescence indicators[29] depends on the principle that salts of organic acids and bases are fluorescent, while the corresponding free acids and bases either are not or else exhibit some other kind of fluorescence.   The analytical importance of these indicators lies especially in the fact that they make it possible to carry out an acid-base titration in colored solutions, where dyestuff indicators cannot be employed.   In the case of fluorescence indicators, as a rule, the cation or anion of the indicator has a fluorescence but not the indicator molecule itself, and the production of the fluorescence depends on constitutional changes which take place concurrently with the dissociation of salts.   Therefore, in this connection, it is interesting to point out a hitherto unknown fact, namely, that the salts of hydroxyquinoline with inorganic and organic acids, which dissociate with production of ammo-

[27] Fr. Krueger, *Ber.* **9**, 1572 (1876).
[28] O. Stark, *Ber.* **40**, 3434 (1907).
[29] Compare I. M. Kolthoff, Acid-Base Indicators, pp. 177–180, New York, 1937.

nium-like cations and the respective acid anions, show no fluorescence in aqueous solution. On the other hand, the solid anhydrous salts, without exception, have a strong fluorescence with a yellow to blue color.[29a] It must, therefore, be assumed that the lattice of these crystalline salts shows fluorescence, but not the hydrated ions of oxine. The fluorescence that appears when boric acid and alizarin are brought together,[30] and also when boric and molybdic acids react with tincture of cochineal[31] show that solutions of acids can produce fluorescence reactions with organic compounds. Eichler,[32] and also Grant and Both,[33] showed that other anions (e.g., nitrite, hyposulfite and sulfite) can be detected, after reaction with organic compounds, by fluorescence effects. Although little material is now available, it seems probable that in inorganic analysis consideration will have to be given not only to the production of fluorescence colors by the formation of organic salts, but also to the possibility that fluorescence may be quenched by salt formation. In this connection it must be mentioned that the fluorescence of uranyl nitrate is extinguished by Cl^-, Br^-, I^-, CN^-, CNS^-, S^{--}, and $Fe(CN)_6^{---}$ ions.[34] Even small quantities of these anions can be detected in the presence of indifferent anions by this quenching.

Goto (loc. cit.) described an interesting quenching of a fluorescence as the result of an addition reaction of iodine. A water solution of α-naphthoflavone gives a blue color with iodine, which is about five times as sensitive as the iodine-starch reaction.[35] In contrast to free α-naphthoflavone, which has a blue fluorescence, its iodine addition compound has no fluorescence. Consequently, the fluorescence of small quantities of naphthoflavone is quenched by the action of iodine. This effect can be used in analysis.

Fluorescence phenomena are much more common with organic compounds and a large number of observations on these have been made.[36] It seems that fluorescence colors, which occasionally are visible even in daylight but that can always be seen in ultraviolet light, may be ascribed to certain groups or certain linkage relationships, or to possibilities of

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[29a] F. Feigl, C. Török and H. W. Zocher, unpublished studies.

[30] L. Szebellédy and S. Tanay, Z. anal. Chem. 107, 26 (1936).

[31] L. Szebellédy and J. Gall, Z. anal. Chem. 98, 255 (1934); L. Szebellédy and F. Jonas, Mikrochim. Acta 1, 46 (1937).

[32] H. Eichler, Z. anal. Chem. 96, 17, 98 (1934).

[33] J. Grant and J. Both, Analyst 57, 514 (1932).

[34] Y. Volmar, Bull. soc. chim. [4] 53, 385 (1933).

[35] J. F. Reith, Pharm. Weekbl. 66, 1097 (1925).

[36] J. de Ment, op. cit., pp. 229–260 gives a comprehensive compilation of fluorescing purely organic compounds, metal salts, organic acids, and dyes, with references to the literature.

tautomeric rearrangements in molecules of organic compounds. However, no generally applicable rules governing this are known, as yet.[37]

The fluorescence analysis of organic compounds has mainly been limited to testing finished products for fluorescence, sometimes after adding acids, alkalies, or salts. This procedure is of great value in the determination of the origin of the samples, and for the detection of impurities, *etc.* The author has pointed out that another essentially different approach gives great promise, namely, the production of a fluorescing compound by a clear cut chemical reaction of two or more organic compounds that, of themselves, do not fluoresce. The appearence of a fluorescence then indicates that the reaction has taken place and consequently certain compounds or groups must be present in the material being tested. All tests based on this principle are sensitive.

Examples of the use of such synthesis of fluorescing compounds are: Detection of 1,2-dicarboxylic acids by fusion with resorcinol to form fluorescent dyes of the fluorescein or saccharine series;[38] detection of citric acid by conversion into the fluorescent ammonium salt of citrazinic acid;[39] detection of NH_2-, NH-, and NCH_3-groups in aliphatic and aromatic compounds, also pyrrole and its derivatives, by conversion into characteristically fluorescing dyes of the rhodamine series after fusion with fluorescein chloride and zinc chloride.[40] These instances show that the new method is practicable for specific and selective tests in numerous cases (compare Chapter VI). Doubtless further cases will be found, particularly since, in principle, the reverse method is possible, namely the extinction of fluorescence through the reaction of the fluorescing compound with another organic material.

When fluorescent compounds are formed by synthesis, care must be taken that the starting materials themselves exhibit no, or only an insignificant fluorescence, and if so, that it is of another kind, when possible. This requirement is not always met completely, because fluorescence can often be caused by even such slight quantities of material that they sometimes cannot be detected by purely chemical methods.[41] It

[37] R. MEYER, *Z. Physik. Chem.* **24**, 468 (1897); H. KAUFMANN, *Sammlg. chem. tech. Vorträge, Stuttgart,* 1907; *Ber.* **50**, 595 (1917); R. KOWALSKI, *Compt. rend.* **151**, 810 (1910); O. MURRIN, *Ber.* **72**, 29 (1939); P. PRINGSHEIM, *Trans. Faraday Soc.* **35**, 29 (1939).

[38] Compare F. FEIGL, Spot Tests, p. 360.

[39] Compare F. FEIGL, Spot Tests, p. 407; F. FEIGL and V. ANGER, *Mikrochemie* **17**, 35 (1935).

[40] Compare F. FEIGL, Spot Tests, pp. 371, 378; F. FEIGL, V. ANGER and R. ZAPPERT, *Mikrochemie* **16**, 67 (1934).

[41] It is quite probable that many organic compounds that have been described as fluorescent, with statement of definite fluorescent colors (see note 36, in reality owe

should also be noted that the filter paper, on which the fluorescent compound may be placed, occasionally exhibits a fluorescence of its own. Furthermore, many varieties of glass glow yellow-green in ultraviolet light and a few, even reddish. It is well to use copper foil, that has been given a superficial uniform coating of black copper oxide by heating in a free flame, as a support for solids. Preparations, and also solutions, that show particularly weak fluorescence should be viewed against black supports or backgrounds. Occasionally white supports are desirable, and filter paper that has been irradiated for several minutes with unfiltered ultraviolet light is suitable for this purpose.[42] If a fluorescence or a change in fluorescence is to be detected in drops of a solution, it is advantageous to use a piece of lead foil, which has been coated with lead sulfide by treatment with ammonium sulfide. The PbS substratum is resistant to dilute, non-oxidizing acids and caustic alkalies.

The fluorescence of the reaction product formed by converting organic compounds into fluorescent materials is usually viewed in aqueous solution, and in glass vessels whose walls should be as thin as possible. Frequently, an increased sensitivity is secured if the test solutions are poured onto filter paper, or are allowed to rise in strips of filter paper, or if the spot zones on the filter paper are observed in ultraviolet light. The examination of such capillary pictures of solutions of a material incited to fluorescence by ultraviolet light, ordinarily results in a far more intensive glow than is exhibited by the compact solid or its solutions. Haitinger[43] believes that this increased intensity of the fluorescent glowing of materials is due to the finer dispersion in the capillaries of the paper. Accordingly, the fluorescence is likewise much greater when the test materials are adsorbed, and thus highly dispersed, on wool, cotton wool, artificial silk, alumina, etc. The fluorescent compounds formed from non-fluorescing components will probably have still better limits of detection if they should be adsorbed on suitable substrates than they exhibit when examined by the present methods.

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this fluorescence, or certain fluorescence colors, to the presence of small amounts of contaminants which could not be detected by the then available chemical or physical methods. Even the hydrocarbon fluorene, which was so named because of its decided fluorescence in daylight, shows this characteristic hardly at all when highly purified [W. R. HODGKINSON and F. E. MATTHEWS, J. Chem. Soc. 43, 163 (1883)]. Chromatographic adsorption seems to provide the only possibility of an exhaustive purification (compare Chapter X). The studies of TH. WAGNER-JAUREGG [Z. physiol. Chem. 239, 188 (1936)] are pertinent. He showed, for instance, that acridine has a blue fluorescence before it is purified by adsorption on alumina, and a yellow fluorescence after such purification.

[42] Compare M. HAITINGER and V. REICH, Z. angew. Chem. 41, 992 (1928).

[43] M. HAITINGER, Die Fluorescenzanalyse in der Mikrochemie, p. 24, Vienna, 1937.

The capillarity effect of paper has been used often because of the increased intensity of the glow shown by fluorescing materials adhering to the paper. The capillary pictures are produced chiefly by allowing solutions to ascend strips of filter paper and the components, which are thus separated by capillarity into different zones, are then tested for fluorescence (*capillary luminescence analysis*). In such cases, typical colors in ultraviolet light may furnish a valuable informational supplement to any colors shown by the respective zones in daylight. Often the capillary rise in strips can be omitted if the capillary picture is produced instead by allowing a drop of a solution to spread, and then examining the paper in ultraviolet light. Rojahn,[44] who coined the appropriate name "drop capillary picture" for this procedure, and also Danckwortt,[45] have reported their results on testing pharmaceutical preparations. Neugebauer,[46] after comparing about forty varieties of absorbent and filter papers, has recommended Schleicher and Schüll Nos. 604 and 587 as particularly suitable for capillary luminescence analysis. The author has found that No. 598g is equally good. Ordinarily, the capillary pictures are best observed when the paper is dry, because the lamp then produces the most intense fluorescence. The observation should always be made with controls and against a non-fluorescing support. When seeking traces by means of capillary pictures, it must always be remembered that even in blank tests with distilled water a small brown zone frequently appears at the upper end of the capillary picture. This zone should not be a decisive factor in coming to a conclusion. Its nature is still unknown.

If drops of a fluorescing solution are placed on filter paper, an adsorptive accumulation of the fluorescing material in definite zones of the fleck may result. An improvement in the discernibility of the fluorescence is thus a possibility. The assumption by the author that an increase of the fluorescence through adsorptive binding may also play a part here, has been tested on fluorescing dyestuffs by Zocher and Török.[47] The behavior of berberin sulfate provided them with an instance which confirmed the assumption and also showed its limitations. When a drop of a water solution of berberin sulfate is placed on lead foil which has been coated with lead sulfide (compare p. 681), the yellow fluorescence can just be seen at a dilution of 1:100,000. However, if a drop of the solution is put on filter paper, a yellow-fluorescing fleck, surrounded by a nonfluorescing water ring, can easily be seen in ultraviolet light at a dilution of 1:200,000,000. This enormous increase in sensitivity cannot

[44] C. ROJAHN, Beiträge zur pharmazeutischen Analyse, Halle, 1937.
[45] P. DANCKWORTT, *Ber. deut. pharm. Ges.* **46**, 184 (1936).
[46] H. NEUGEBAUER, *Pharm. Ztg.* **74**, 1511 (1929).
[47] H. W. ZOCHER and C. TÖRÖK, unpublished studies,

be ascribed to a mere local accumulation of the dyestuff. Probably, a more strongly fluorescing form of the berberin sulfate has been adsorbed in the capillaries of the filter paper (compare p. 612). This assumption is supported by the finding that no such differences are observed when the same experiment is conducted with solutions of this salt in acetone, alcohol, amyl acetate, *etc.* In these latter instances, the fluorescence can be discerned on the lead foil at a dilution of 1:30,000,000, and there is no significant enhancement of the sensitivity on filter paper.

Considerable analytical value attaches to the identification of organic materials through an eventual fluorescence of materials separated by a chromatographic procedure (see Chapter X). In this, the parts of a mixture of dissolved compounds are separated from each other by fixation in definite zones of an adsorption column. For example, Winterstein,[48] and also Karrer,[49] were able to detect colorless adsorption zones of fluorescing materials by examining them under ultraviolet light. Karrer coined the term "ultrachromatography" for this method. Chromatography also makes it possible to keep the individual members of mixtures of dissolved fluorescing compounds apart by holding them in distinct zones of the adsorption column, in order that a mixed fluorescence can be broken down into the true fluorescences of the components of the original mixture. In addition to the alteration of fluorescence colors in mixtures, there seems also to be a possibility of a kind of masking of fluorescence colors by the accompanying materials. For instance, the presence of as little as 1/30,000% of naphthazene is enough to obliterate completely the beautiful blue fluorescence, exhibited under ultraviolet light, by anthracene and its solutions.[50] In this case also, the characteristic fluorescence of anthracene can be restored by a chromatographic separation of the mixture; this represents a sort of demasking. These examples were selected particularly because they demonstrate that fluorescence analytical tests can be made quite specific by combination with chromatographic separations. In this connection, it should also be pointed out that sometimes the same compound may exhibit different fluorescences if it is fixed on various adsorbents. Thus, benzanthrone fluoresces golden yellow in benzene solution; fixed on $CaCO_3$ or Al_2O_3 the fluorescence is canary yellow, but when adsorbed on natural Fuller's earth it fluoresces green, and on artificial bleaching earth the color ranges from golden yellow to red-orange.[51] Grassmann and Lang[52] found that

[48] A. WINTERSTEIN, *Z. physiol. Chem.* **230**, 139 (1934).

[49] P. KARRER, *Helv. Chim. Acta* **17**, 693 (1934).

[50] Taken from E. HESSE, Adsorptionsmethoden in chemischen Laboratorium, p. 89, Berlin, 1943.

[51] H. CARLSON and G. MUELLER, *Ber.* **71**, 858 (1938).

[52] W. GRASSMANN and O. LANG, *Collegium* **1935**, 114, 401.

the same compound may exhibit various fluorescence colors depending on whether it is tested in the solid, dissolved, or adsorbed condition.   Solid phloroglucinol has a luminous blue-green fluorescence; the solution fluoresces more toward the green; adsorbed on Al_2O_3 the fluorescence is yellow.   An alteration of the fluorescence colors by certain adsorbents, and likewise a quenching (masking) of these colors may possibly be applied some day for analytical purposes.   The fact that fluorescence colors are sometimes strongly and characteristically dependent on the prevailing pH values[53] will surely·be of interest when aqueous solutions are being studied or subjected to ultrachromatographic analysis.

The separation and local fixation of dissolved materials by adsorption in definite zones of paper or adsorption columns are important aids in securing microchemical sensitivity and extensive selectivity in fluorescence analytical tests.   Fluorescence occurs most often among organic compounds, and products with characteristic fluorescence characteristics can sometimes be prepared from non-fluorescing materials (see p. 680). Hence, it can be expected, and experience has already shown in some cases, that the chief field of application of fluorescence in analytical chemistry will be qualitative organic analysis.   Among fluorescing organic compounds that are capable of producing normal and complex salts, the isolation of fluorescing salts may contribute to increasing the specificity, selectivity, and sensitivity of fluorescence tests.   The statements on p. 677 indicate that the formation of such salts can likewise be of value in inorganic analysis.   However, this constitutes analysis, in the strict sense, only when definite and chemically defined compounds are identified by means of a characteristic fluorescence.   In technical examinations of inorganic and organic industrial products, the establishment of a fluorescence and a comparison of fluorescence colors are used to derive conclusions as to whether products are identical, or whether they have a common origin.   Likewise, fluorescence analysis provide rapid procedures for detecting admixed materials or traces of contaminants.   In such cases, and especially when testing organic products, it is not possible on the basis of chemical reactions to state definitely the nature of the fluorescing constituent or of the material that is exciting the fluorescence.   Under such circumstances, the establishment of a fluorescence, the emission of similar fluorescence colors, or the failure of a fluorescence to appear, are used simply as empirical comparison methods, which, none the less, can often be of extraordinary utility.

Fluorescence analysis utilizes the light rays of characteristic wave lengths given off by compounds that are being exposed to visible or ultraviolet light.   A chemical change of the fluorescing material is never

⁵³ Compare W. KOSCHARA, *Z. physiol. Chem.* **240**, 127 (1936).

occasioned by this treatment. However, the mutual actions between light energy and chemical energy are also of some importance for analytical purposes. These actions can be of two kinds: (a) the causing or acceleration of chemical processes by light, or (b) the emission of light during the course of chemical changes. With regard to photochemical processes of the first type, numerous examples are known in which light exerts an effect on many kinds of chemical reactions exhibited by inorganic and organic compounds, and on reactions of materials in all states of aggregation. Furthermore, it has long been known that reagents frequently decompose on standing in the light. Consequently, it is somewhat surprising that the number of instances is extremely small, in which there has been a direct deliberate employment of photochemical reactions for the detection of inorganic or organic compounds. This may be due in part to the fact that analytically important reactions are invariably carried out in daylight or under ordinary artificial illumination. There has been no experience in conducting these reactions in the dark, because this procedure has had no practical interest. Consequently, there is no available information as to whether or not some of these procedures would give significantly different results in the dark.

The following discussion deals with certain photochemical processes that bear on the problems emphasized in this book, namely, the specificity, selectivity, and sensitivity of tests. The so-called primary processes are fundamental for photochemical changes in which light is converted into chemical energy. According to now well established views, this process consists of the absorption of quanta of light energy by a molecule or atom of a light-absorbing and photochemically active system. The process can be represented symbolically: $AB + h\nu \rightarrow AB^*$. In this expression, AB^* is the molecule that is activated and richer in energy; h is a universal constant; ν is the frequency or vibration number of the light; $h\nu$ represents a quantum of light. This primary process is then followed by physical or secondary processes in which AB^* appears as an active participant. The life of the activated molecule is always short, a fact of importance for any chemical secondary processes which may occur along with physical secondary processes. Of further significance is the fact that fundamentally no reaction is possible which requires a supply of energy greater than the energy content of the excited molecule.

Equilibrium systems, in which one reaction partner can be activated by light, are of special practical importance from the analytical standpoint. The absorption of light, in such cases, can shift the equilibrium, and this change persists as long as the irradiation is continued. This is known as a photochemical equilibrium or stationary (steady) state. Such photochemical equilibria, and disturbances of them by removal of

their resulting products, are often the cause of the decomposition of reagents. Pertinent examples are: the decomposition of water solutions of hydrogen sulfide, hydrogen peroxide, chlorine, alkali ferrocyanide and ferricyanide, silver salts, the decolorization· of alcohol solutions of ferric chloride, *etc.* Such photochemical decompositions also proceed when filter paper impregnated with certain reagents is stored. The action of light and air is especially marked in such cases because the reagents are so finely dispersed in the capillaries of the paper. For instance, sodium rhodizonate paper, used for the detection of barium and lead (see p. 174), keeps only if it is stored dry, and out of contact with air. If moist rhodizonate paper is illuminated, particularly under a quartz lamp, decomposition, with bleaching of the original yellow brown paper, proceeds so rapidly that this experiment can actually be used as a lecture demonstration of photodecomposition. The stability of reagents and of reagent papers patently is of great importance to the sensitivity of tests. This factor is particularly significant in spot test analysis where impregnated filter papers (see p. 654) play a leading part in attaining the maximum sensitivity. The fading of colored reaction products, so frequently observed in spot tests on paper, belongs in this category. This instability is especially detrimental if the flecks need to be preserved for future reference. Ultraviolet rays are particularly responsible for such fading.[54]

Sometimes it is necessary to consider also the possibility of a photochemical decomposition of solid products[55] and of solutions that are to be subjected to an analysis. Obvious examples are the compounds just cited as light-sensitive reagents. An additional instance is provided by the interesting finding of Mack and Hamilton.[56] ˉThey observed that solutions of sulfur in acetone, dioxane, and butylcarbitol (monobutyl ether of diethyleneglycol) remain unchanged in the dark. When exposed to direct sunlight or ultraviolet light, the sulfur reacts in some as yet unexplained manner with the solvent. For example, if 200γ sulfur is dissolved in 100 ml. of acetone and the solution irradiated with ultraviolet light, 80% of the sulfur disappears in 20 minutes, *i.e.*, it is no longer

[54] C. SCHALL [*Chem. Ztg.* **34**, 267 (1909)] has described a reagent paper for detecting ultraviolet light. Filter paper impregnated with $\frac{3}{5}N$ *p*-phenylenediamine nitrate, and then dried, is sensitive only to wave lengths shorter than 3130 Å. Consequently, exposure to daylight produces only a pale gray tint, but the light from a mercury lamp turns the paper blue at once.

[55] The presence of moisture seems to be important to the photochemical decomposition of solids. This can be deduced from the fact that AgCl, the classic prototype of light-sensitive materials, is absolutely light-stable in the absence of moisture and of substances that serve as acceptors of free chlorine. See the interesting study by H. B. BAKER, *J. Chem. Soc.* **61**, 735 (1892).

[56] G. L. MACK and J. M. HAMILTON, *Ind. Eng. Chem., Anal. Ed.* **14**, 605 (1942).

convertible into colloidal copper sulfide when treated with an ammoniacal copper solution. They used the formation of colloidal copper sulfide as the basis of a photometric method for estimating small amounts (up to 1 mg. in 10 ml.) of free sulfur dissolved in acetone..

Photochemical processes have long been known with respect to the decomposition of analytical reagents. Such deterioration must be guarded against and can often be prevented by suitable measures. Usually storing in the dark is sufficient. In certain cases, light-sensitive reagent solutions (perhaps reagent papers also) can be stabilized by adding the proper materials. For instance, the addition of as little as 0.05% phenacetin (p-acetophenetidine) will prevent the decomposition (with formation of nitrobenzene) of water solutions of cupferron (see p. 262) exposed to sunlight.[57]

The planned use of photochemical processes to attain certain objectives in qualitative inorganic and organic analysis is rather new. The earliest instance in qualitative inorganic analysis was due to Velculescu.[58] He showed that the fundamental process of photography, namely the formation of silver nuclei when silver halides are exposed (latent image), can be adapted to provide the most sensitive test known for silver. A drop of the diluted silver test solution is placed on filter paper, which is then bathed in potassium bromide solution. After washing, the fleck, that possibly contains silver bromide, is treated with a freshly prepared developing solution that contains silver nitrate. If the fleck contains silver nuclei, metallic silver will be deposited on these centers, as a result of the so-called physical development. A black stain is produced. The detection of 0.005γ Ag (1:10,000,000) is possible by this means. Feigl[59] found that the various halide ions can be detected by utilizing the photolysis of AgCl, AgBr, and AgI. On exposure they are decomposed: AgHal → Ag + Hal. The finely divided silver halide, which still contains minute quantities of adsorbed Ag^+ ions, is exposed to ultraviolet light. A photohalide is produced, and can be seen easily because it gives a brown or black coloration. These photohalides consist of unchanged silver halide containing finely divided or adsorbed silver. Active silver halide is obtained by placing a neutral or acetic acid solution of a halide on paper impregnated with silver chromate.[60] The paper is then irra-

[57] F. G. GERMUTH, Chemist-Analyst 17, 7 (1928).

[58] A. J. VELCULESCU, Z. anal. Chem. 90, 111 (1932).

[59] F. FEIGL, Laboratory Manual, p. 112. See also the interesting study of the photolysis of silver chloride from the analytical standpoint by G. E. F. LUNDELL and J. I. HOFFMAN, Bur. Standards J. Research 4, 109 (1930).

[60] Silver chromate paper is prepared by bathing the paper in an ammoniacal solution of Ag_2CrO_4. The paper is then dried to remove the ammonia.

diated briefly, to fix any halide as photohalide. The unused silver chromate is then dissolved out with ammonia. The silver photohalide remaining on the paper always retains some adsorbed silver ions. On irradiation with a quartz lamp, more photohalide forms and produces a brown fleck or ring. This method, as a spot reaction, will reveal as little as 3γ Cl^-, Br^-, or I^-.

Sharma[61] made analytical application of a photochemical reaction with an enormous sensitivity. Its chemical basis has not been clarified satisfactorily. If even traces of ferrous or ferric salts are added to a saturated solution of ammonium thiocyanate, and the mixture is irradiated, a reddish tint develops in the solution. This color disappears if the solution is placed in the dark.[62] Both the intensity of the coloration and the time required for its disappearance are proportional to the concentration of iron. The effect can still be observed with 10^{-11} g. of iron. Sharma assumes that an addition compound, $Fe(CNS)_3 \cdot O_2$, is formed, and that this decomposes in the dark. Consequently, a photochemical equilibrium would be involved.[63]

The light-sensitivity of a reaction product sometimes lowers the sensitivity of a test. An instance of this is provided by the well-known sodium nitroprusside test for alkali sulfides. A violet solution is produced as a result of the reaction:

$$Na_2[Fe(CN)_5NO] + Na_2S \rightarrow Na_4[Fe(CN)_5(NO)S]$$

Vogel[64] found that the violet solution rapidly loses its color in sunlight. The complex-bound alkali sulfide seems to be oxidized to sulfate more rapidly than when alone. If the test is made in direct sunlight the result, especially in dilute alkali sulfide solutions, is a rapid lightening or disappearance of the violet coloration. This, of course, means a lowering of the sensitivity of this test. A familiar photodecomposition (photolysis) is encountered with ferric thiocyanate. The fading of the red solutions is due to a reduction of the iron, and also to oxidation of the thiocyanate radical. These actions are hastened by illumination. This photosensitivity must be taken into account in colorimetric determinations of iron, and in the preparation of $Fe(CNS)_3$ comparison solutions.

[61] B. S. SHARMA, J. Chem. Soc. (London) 133, 308 (1930).

[62] This effect was first observed by R. LIESEGANG with NH_4CNS and $Al(CNS)_3$, that apparently contained iron. Jahrb. Photographie 49, (1894).

[63] This view is controverted, however, by the fact that the photo-effect does not occur in KCNS solution. Perhaps the formation of thiourea, an isomer of NH_4CNS, plays a role.

[64] A. VOGEL, Phot. Mitt. 7 (1882). According to A. CASOLARI [Chem. Ztg. 38, 541 (1914)] the blue color produced by bringing together $Na_2[Fe(CN)_5NO]$ and $Na_2S_2O_3$ is likewise destroyed by exposure to light.

It is noteworthy that the red coloration produced by bringing together ferric and salicylate ions in weakly acid solution bleaches in sunlight. This color reaction is due to the formation of inner complex anions which contain Fe^{III} and salicylate radicals. If the discharge of the color is due to a redox reaction that is accelerated by light, analogous light-sensitivity may be expected in other color reactions of iron with polyphenols. Nothing is known about such light sensitivity of these or other inner complex metal-bearing anions.

A converse of undesirable photolyses is the deliberate photolysis of a material that is to be detected through the subsequent identification of its decomposition product. The only known instance of this is the procedure developed by Steiger[65] for the detection of lead tetraalkyls and nickel carbonyls (anti-knock materials). A drop of the sample is placed on filter paper and irradiated briefly under a quartz lamp. Decomposition ensues[66] and the traces of lead or lead hydroxide deposited at the site of the fleck can be identified by either the sensitive dithizone reaction or by the rhodizonate reaction. The nickel can be detected with dimethylglyoxime.

An interesting example of a reaction, which for useful analytical purposes has sufficient velocity only in light, is the test recommended for organic nitroso compounds (see p. 377) by Feigl and his co-workers.[67] The prussic salts, $Na_3[Fe(CN)_5NH_3]$, and $Na_3[Fe(CN)_5H_2O]$ serve as reagents here. The light yellow aqueous solutions of these two salts give intense green or violet colorations with solid nitroso compounds or their alcohol solutions. Small quantities of nitroso compounds can be detected in this way, and likewise nitro compounds after reduction, which is easily accomplished. Furthermore, tertiary aromatic bases, with a free *para* position, can be detected, after nitrosation with nitrous acid.[68] According to Baudisch,[69] the reaction of the prussic salts with nitroso compounds can be represented:

$$Na_3[Fe(CN)_5X] + RNO \rightarrow Na_3[Fe(CN)_5RNO] + X \; (X = NH_3 \text{ or } H_2O)$$

Accordingly, this involves a displacement reaction in the solution of a complex salt, and as Baudisch proved, it occurs only in the light. Consequently, when this reaction is used, it is well to illuminate the reaction mixture under a quartz lamp. Baudisch also made the interesting observation that the addition of pyridine prevents the photoreaction

[65] B. STEIGER, *Petroleum* **27**, 33 (1937); *Mikrochemie* **22**, 22 (1937).

[66] H. KIEMSTEDT, *Z. angew. Chem.* **42**, 1107 (1929).

[67] F. FEIGL, V. ANGER and O. FREHDEN, *Mikrochemie* **16**, 181, 183 (1934).

[68] F. FEIGL, unpublished studies.

[69] O. BAUDISCH, *Ber.* **54**, 413 (1921).

between prussic salts and nitroso compounds, whereas α-picoline does not. The reason for this masking is that pyridine enters the prussic salt in place of the ammonia or water molecule. It is more firmly bound by coordination to the iron atom than was the original predecessive NH_3 or H_2O molecule. This restraining of the photoreaction of the prussic salts can be utilized to detect pyridine in α-picoline.

Primary aromatic amines, also aliphatic and aromatic hydrazines, likewise displace water or ammonia from prussic salts. Since colored products result, as in the test for nitroso compounds, such amines and hydrazines can be detected by this reaction.[70] However, unlike the displacements by nitroso compounds, these reactions are not sensitive to light.[71] Consequently, since there is a specific light effect in the former case, it must be concluded that the illumination produces excited RNO* molecules rather than activated molecules or ions of the prussic salt.[72]

Baudisch[73] also showed that potassium ferrocyanide, under illumination, acts toward organic nitroso compounds as prussic salts do. The reaction is:

$$K_4[Fe(CN)_6] + RNO \rightarrow K_3[Fe(CN)_5RNO] + KCN$$
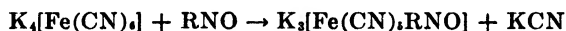
A molecule of KCN is displaced, with formation of the same complex anion that is produced by the photoreaction of prussic salts with nitroso compounds. It is interesting that the reverse reaction occurs if potassium cyanide is added to the colored nitroso compound and the mixture then illuminated.

Lund and Lieck[74] described a method for the detection and determination of ascorbic acid (vitamin C), which is based on the photoacceleration of a redox reaction. In this, methylene blue is reduced to the colorless leuco base by ascorbic acid. The reduction is extremely slow in the dark, but at low pH values it is so greatly accelerated by ultraviolet light that even 0.1% ascorbic acid can be detected. These workers report that

[70] F. FEIGL, V. ANGER and O. FREHDEN, *Mikrochemie* **15**, 184 (1934); V. ANGER, *Mikrochim. Acta* **2**, 3 (1937).

[71] F. FEIGL, unpublished studies.

[72] A. KUTZELNIGG [*Z. anal. Chem.* **77**, 349 (1929)] has made the interesting observation that the addition of isobutyl alcohol to a solution containing a prussic salt or sodium nitroprusside gives an orange-red coloration on illumination. This effect probably involves a reaction mechanism analogous to that of the displacement reactions discussed in the body of the text. It is quite remarkable that *n*-butyl alcohol and other alcohols do not show this color reaction. Consequently, crude alcohol prepared from potatoes can be definitely distinguished from that made from beets, since the former will give a positive reaction by this test for isobutyl alcohol, whereas the crude spirits from beets give a negative reaction.

[73] O. BAUDISCH, *Ber.* **54**, 413 (1921).

[74] H. LUND and H. LIECK, *Nature* **137**, 784 (1936).

quantitative estimates of ascorbic acid are possible through comparison of the discharge time with that of a given amount of methylene blue.

Aloy and his co-workers[75] discovered a valuable photochemical reaction for the detection of strychnine, codeine and morphine. It is based on the fact that these alkaloids, if dissolved in concentrated sulfuric acid, give characteristic colors in the presence of uranyl acetate. Strychnine gives a violet, codeine and morphine a blue color.[76] No other ordinary alkaloid gives a similar reaction. This test, in the form of spot reactions, has an identification limit of 10γ alkaloid. The exact mechanism is not known. However, it is certain that the formation of formaldehyde, through photolysis of uranyl acetate, plays a part. The discovery of this fact made it possible for these workers to carry out the alkaloid tests without illumination; they merely added a little formaldehyde. Furthermore, they recommended a solution of codeine and uranyl acetate, in concentrated sulfuric acid, as a sensitive reagent for formaldehyde. In this connection, a fact, first observed by Freytag and Neudert,[77] should be mentioned. They found that filter paper impregnated with pyridine and certain of its derivatives, after irradiation with ultraviolet light, gives characteristic color reactions with primary aromatic amines. Feigl and Anger[78] proved that the effect is due to the production of unsaturated glutaconic aldehyde on photolysis of the pyridine. The aldehyde then reacts with primary aromatic amines, forming colored Schiff's bases. After this elucidation of the mechanism of the photo-pyridine reaction, the readily available glutaconic aldehyde could be recommended as a specific reagent for primary aromatic amines.[79] These reactions with alkaloids and primary aromatic amines showed that it was possible, through partial or complete clarification of the chemistry of photoreactions, to develop new tests that proceed without the action of light. This is a consequence of the basic fact that no new reaction can be created by illumination, and the action of light can do no more than bring about such changes as can also be accomplished by other means. Hence, it is plain that photoreactions can be of interest to the analyst for two reasons. First, they can be used directly, and secondly, because, as has been shown, they can call attention to new specific and selective, as well as sensitive test reactions.

The previous examples of photoreactions were based almost entirely

[75] J. ALOY, A. VALDIGUIÈ and R. ALOY, *Bull. soc. chim.* **39**, 792 (1926).

[76] So far as can be gleaned from the literature, this is the first analytical use of a photoreaction in qualitative organic analysis.

[77] H. FREYTAG and P. NEUDERT, *J. prakt. Chem.* **135**, 15 (1932).

[78] F. FEIGL and V. ANGER, *J. prakt. Chem.* **139**, 180 (1934).

[79] F. FEIGL, V. ANGER and R. ZAPPERT, *Mikrochemie* **16**, 74 (1934).

on the initiation or acceleration of chemical processes by light. The inverse process, namely, the emission of rays during the course of chemical changes, also has analytical interest. This photochemical process is known as *chemiluminescence*. Instances of its employment in analysis are also available. The first, and for a long time, the only known case was the "Mitscherlich test" for phosphorus, *i.e.*, the glowing of phosphorus that had been steam distilled out of a mixture. This chemiluminescence is due to the autoxidation of phosphorus, and the sensitivity of this test is high. All other instances of the use of luminescence reactions for analytical purposes are of rather recent date. Schmatolla[80] observed that hydrogen generated from zinc and hydrochloric acid in the presence of soluble or insoluble tin compounds confers a characteristic blue color on the non-luminous flame of the Bunsen-type burner. This luminescence reaction provides a sensitive test for tin;[81] its chemical basis has not yet been explained satisfactorily. Antimony, bismuth, or manganese salts, in contact with a hydrogen flame, give exceedingly sensitive luminescence reactions. The flame with bismuth is blue, with antimony, green blue, and with manganese, yellow. Donau[82] recommends that a hydrogen flame be impinged upon a mixture of the test material and very pure alkaline earth carbonate. In this way, 0.004γ Bi can be detected, or even 0.0001γ Bi, if a parallel test is made. All the studies along this line prove that luminescence reactions are particularly sensitive. This is shown also by the work of Albrecht.[83] He thoroughly investigated the chemiluminescence accompanying the oxidation of 3-aminophthalhydrazide (luminol) with hydrogen peroxide. Steigmann[84] found that the prevention of the luminol-hydrogen peroxide reaction by traces of an ammoniacal copper solution will reveal copper even at a dilution of $1:10,000,000$. Langenbeck and Ruge[85] have used the luminescence of the luminol reaction with hydrogen peroxide in the presence of hemin as activator, as a test for hydrogen peroxide. This will reveal 0.012γ H_2O_2 in one drop.

The number of known chemiluminescence reactions is vanishingly small in comparison with the tremendous number of observations of the chemical action of light. It may be expected, therefore, that new

[80] O. SCHMATOLLA, *Chem. Ztg.* **25**, 468 (1901).

[81] Compare H. MEISSNER, *Z. anal. Chem.* **80**, 247 (1930); F. L. HAHN, *ibid.* **82**, 113 (1930); F. FEIGL, Spot Tests, p. 88.

[82] J. DONAU, *Monatsh.* **34**, 949 (1913); compare also F. EMICH, Lehrbuch der Mikrochemie, 2nd Ed., Berlin, 1926, p. 153.

[83] H. O. ALBRECHT, *Z. physik. Chem.* **136**, 321 (1928).

[84] A. STEIGMANN, *Phot. Ind.* **85**, 1365 (1937).

[85] W. LANGENBECK and V. RUGE, *Ber.* **70**, 367 (1937).

instances of photoreactions that can be used for analytical purposes will be sought primarily among light-sensitive reaction systems.

Because of its close connection with modern physics, especially atomic theory, quantum theory, and spectroscopy, photochemistry has become a separate branch of study, with an extensive literature of its own. Excellent presentations of the field are available in: G. K. Rollefson and M. Burton's, Photochemistry and the Mechanism of Chemical Reactions, New York, 1942, and C. Ellis and A. A. Wells, The Chemical Action of Ultraviolet Rays (revised by F. Heyroth), New York, 1941.

An extremely large literature is now available despite the relatively short time since the fluorescence phenomena have entered into the science of analytical chemistry. A review of the whole field is given in the books: P. Danckwortt, Luminescenzanalyse im filtrierten ultravioletten Licht, Leipzig, 1934; J. Radley and J. Grant, The Analysis in Ultraviolet Light, London, 1930.

Luminescence capillary analysis is discussed in the little book by H. Neugebauer, Die Kapillar-Luminescenzanalyse im pharmazeutischen Laboratorium, Leipzig, 1930.

Microchemical problems and purely chemical facts are discussed at length in the excellent book by M. Haitinger, Die Anwendung der Fluorescenzanalyse in der Mikrochemie, Vienna-Leipzig, 1937.

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